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Page	Line	
ii. 298	10	*for* "**Rusting**" *read* "**Roasting.**"

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ERRATA.

Vol. 117 (Trans., 1920).

Page.	Line.	
475	13	for "s" read "S."
„	14	„ "$9\eta s$" *read* "$9\eta S$."
„	2*	„ "0·15 cm." *read* "0·1588 cm."
476	1	
„	15	
478	10	„ "6·69" *read* "6·69 × 19·4."
661	12	„ "sodium sulphate" *read* "sodium hydrogen sulphate."
832	6	„ "lead acetate" read "sodium plumbite."

Vol. 114 (Abstr., 1918).

ii. 366	20	*for* "tetradimite" *read* "tetradymite."
„	„	„ "grunlingite" *read* "grünlingite."

Vol. 116 (Abstr., 1919).

ii. 337	14*	for "*Aktiebolsg*" read "*Aktiebolag.*"

Vol. 118 (Abstr., 1920).

ii. 441	23	*for* "Ütö" *read* "Utö."
„	„	„ "*Foren.*" read "*Fören.*"
„	25	„ "$p>v$" read "$\rho>v$."
„	27	„ "33·54" *read* "33·64."
„	„	„ "104·27 *read* "104·37."

* From bottom.

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ERRATA.

VOL. 117 (TRANS., 1920).

Page.	Line.	
345	21*	*for* "oxide, a little water" *read* "oxide and a little water."
348	6*	„ "citronellal" *read* "citronellol."
350	2	„ "pæonal" „ "pæonol."
1024	6*	„ "positive" „ "negative."
1026	16*	the formula should be "$3K_3[Fe(CN)_6].K_2[Fe(CN)_5H_2O]$."

VOL. 118 (ABSTR., 1920).

ii 503	11*	*for* "Contact with hydrogen, owing to surface combustion, raises the temperature of one helix," *read* "Contact with hydrogen, owing to the change in thermal conductivity of the gas, lowers the temperature of one helix."

* From bottom.

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ERRATA.

Vol. 112 (Abstr., 1917).

Page. Line.
i. 277 4 *for* "**3:6-dimethyl-1:4-benzopyrone**" *read* "**3:6-dimethyl-2:3-di-hydro-1:4-benzopyrone.**"
,, 13 for "3:6-*dimethyl*-1:4-*benzopyrone*" read "3:6-*dimethyl*-2:3-di-*hydro*-1:4-*benzopyrone*."

Vol. 117 (Trans., 1920).

1276 22 *for* "N = 17·37. $C_{13}H_{10}O_6N_4$ requires N = 17·73"
read "N = 16·35. $C_{20}H_{19}O_6N_5$ requires N = 16·47."

Vol. 118 (Abstr., 1920)

i. 207 1 *for* "**Potassium**" *read* "**Calcium.**"
,, 3 ,, "Potassium" ,, "Calcium."

LXXXIX.—*The Viscosity of Solutions of Nitrocellulose in Mixtures of Acetone and Water.*

By Irvine Masson and Robert McCall.

The viscosity of sols of "soluble" nitrocellulose in ether–alcohol mixtures has been studied by Gibson and McCall (*J. Soc. Chem. Ind.*, 1920, **39**, 172T). The work summarised in the present paper deals mainly with mixtures of nitrocellulose with acetone, pure and aqueous, which are of interest from the point of view of their behaviour as typical colloidal solutions.

The viscosimeter used was that designed by Gibson and Jacobs (this vol., p. 473), in which is measured the rate of fall of a small sphere through the solution.

For the experiments with dry nitrocellulose in anhydrous acetone, it is necessary to dry the solvent by prolonged contact with calcium chloride, followed by fractional distillation with exclusion of water vapour, owing to the marked effect of traces of moisture on viscosity. It is noteworthy that the crystalline compound formed between acetone and calcium chloride (compare Bagster, T., 1914, **105**, 494), which is soluble in anhydrous acetone, has a very marked effect in coagulating sols of nitrocellulose; thus acetone fully dried over calcium chloride, but separated from it by filtration alone, formed with 5 per cent. of nitrocellulose a stiff jelly having an apparent viscosity of 5000 C.G.S. units, whereas when separated from the calcium chloride by distillation, the acetone gave a mobile sol, the viscosity of which was 13 units. The presence of a little water largely counteracts this coagulating effect, whence it appears that hydrated calcium chloride differs in this respect from the acetone compound. This might repay investigation from the point of view of the coagulation of aqueous sols by electrolytes.

Change in Viscosity with Time.

For consistent results to be obtained, the mixtures must be made up with the aid of very vigorous initial agitation, followed by mechanical shaking, until uniformity of composition is attained; and in studying these conditions, it was found that there is a very slow decrease of viscosity with time, even after the shaking is ended. With ether–alcohol sols, a much more rapid effect in the opposite direction was observed by Gibson and McCall

(*loc. cit.*), and such changes have often been noticed with other colloidal systems.

Further measurements have therefore been made with acetone and with mixtures of ether and alcohol. With acetone, either anhydrous or aqueous, the viscosity rises rapidly within a few minutes of mixing to a maximum value, and then falls very gradually, and the same is found to be true with the particular mixture of ether and alcohol in which the nitrocellulose has its lowest viscosity. The more widely, however, the composition of this solvent deviates from this "optimum" value, the longer is

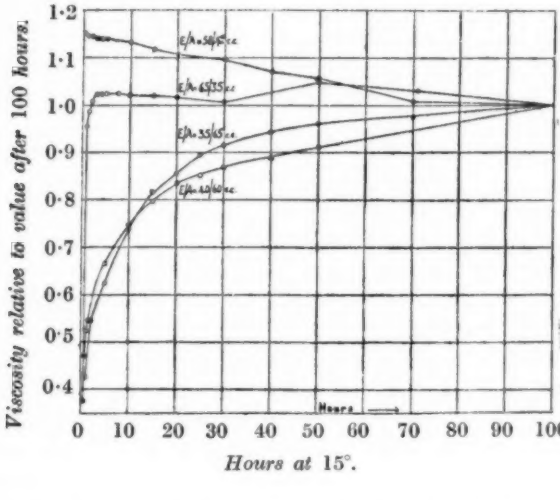

FIG. 1.—*Change of viscosity with time at* 15°. *Nitrocellulose* (N = 12·2 *per cent.*) 6 *grams; ether-alcohol* 100 *grams.*

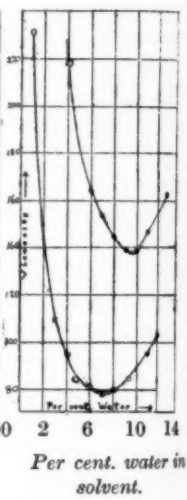

FIG. 2.—*Effect of water on viscosity in acetone. Nitrocellulose* 10 *grams; solvent,* 100 *grams.*

the time taken by the solution to arrive at its highest viscosity. These facts are illustrated in Fig. 1.

It appears that two processes are at work, first, the absorption of solvent by nitrocellulose, accompanied by the dispersion of the resulting gel; secondly, a change in the already dispersed gel, which may probably be ascribed to a change in the state of aggregation of the particles, not necessarily accompanied by any alteration in their percentage composition. With acetone, and with ether–alcohol near the "optimum," the former process is very rapid; with other ether–alcohol mixtures the absorption of solvent, with resulting swelling of the particles and decrease in the volume

of the surrounding fluid, continues for some time, even after the primary dispersion has occurred. In all cases, the second process is very slow.

Influence of Water on Viscosity.

Measurements were made at 20° of the viscosities of a number of kinds of nitrocellulose in acetone to which varying proportions of water had been added; some typical results at various concentrations are shown in table I and in Fig. 2. It will be seen that the viscosities in anhydrous acetone are relatively very high, and that

TABLE I.

Absolute Viscosities at 20° in Acetone and Water.

Concentrations in grams per 100 grams of acetone and water. Italicised numbers show minimum viscosities.

Percentage of water.	N=12·3 per cent.				N=13·0 per cent.		
	5.	7.	8·5.	10.	5.	7.	10.
0	—	—	—	—	12·5	—	—
1	34·2	213·2	—	—	8·8	32·0	232
2	—	—	—	451	—	26·4	—
3	11·7	62·5	157·3	—	6·1	—	110
4	—	—	—	218	6·0	20·8	96·4
5	8·6	41·4	90·5	—	6·0	—	83·3
6	8·2	36·7	74·6	164	*5·9*	*20·2*	81·1
7	8·0	33·8	73·8	154	*5·9*	20·7	*79·3*
8	*7·9*	32·9	72·5	144	*5·9*	21·4	79·7
9	*7·9*	*32·7*	*69·3*	138	—	23·0	83·3
10	8·1	35·5	71·4	*138*	6·6	24·6	—
11	8·0	—	72·7	147	—	—	94·9
12	—	36·6	75·7	—	7·3	28·2	103
13	9·1	—	79·9	163	7·1*	—	120
14	—	40·2	—	—	—	—	—
15	8·6	—	—	154*	—	—	—
16	—	47·6*	—	—	—	—	—

* Miscibility incomplete.

traces of water have a most marked effect in lowering viscosity. The influence of water diminishes with further addition, until in mixtures still more aqueous the viscosity again rises. There is thus an optimum solvent composition at which the viscosity is at a minimum. When upwards of 12 per cent. of water is present in the acetone (the exact figure depending on the type and concentration of nitrocellulose), the liquid will no longer permit the dispersion of the nitrocellulose, but it still causes gelatinisation, to an extent depending on the water-content. The optimum solvent-composition (by make-up) is not the same for all kinds of nitro-

cellulose, nor is it quite independent of concentration. With sols in pure acetone, no appreciable concentration of dissolved matter was detected by ordinary vapour-pressure measurements, and the disperse phase presumably consists of particles of nitrocellulose gel containing absorbed solvent. The proportion of liquid dissolved by nitrocellulose is large; gels collected from highly aqueous acetone contained more than six times as much liquid as solid, whilst other tests showed still greater absorption with mixtures capable of dispersing the material.

Not only the quantity, but also the composition of the absorbed fluid, is found to be affected by the composition of the binary solvent; selective absorption by the gel is at work, hence the composition of the fluid phase at equilibrium is not necessarily the same as that of the solvent before admixture with nitrocellulose. These factors play a leading part in determining the viscosity of such systems as are here dealt with; their quantitative influence has yet to be studied.

Influence of Concentration on Viscosity.

The correlation of the viscosity of sols with the concentration of the disperse phase has attracted the attention of numerous workers; Einstein, also Hatschek (*Trans. Faraday Soc.*, 1913, **9**, 80, with list of references), have obtained an equation founded on theoretical considerations, whilst Arrhenius (*Biochem. J.*, 1917, **11**, 112) has successfully applied an empirical logarithmic expression to numerous cases in which the Einstein-Hatschek expression fails. Baker (T., 1913, **108**, 1653) studied dilute sols of nitrocellulose in acetone, and his data were examined by Arrhenius.

In table II are given some of the results now obtained. Examination of the data shows that none of the equations referred to is applicable except over small ranges, and this is true whether anhydrous or aqueous acetone be used as the solvent. It should be added that Hatschek's second expression (*loc. cit.*), for cases where the disperse phase occupies most of the total volume, does not apply to the present data, and, indeed, it cannot hold for any case in which the viscosity is great compared with that of the solvent.

TABLE II.

Viscosities at 20° in Anhydrous Acetone.

Nitrocellulose, N = 13·0 per cent.			Nitrocellulose, N = 12·2 per cent.	
Grams per 100 grams of acetone	D_4^{20}.	Viscosity (absolute).	Grams per 100 grams of acetone.	Viscosity (absolute).
—	0·792	0·0033*	—	—
0·63	0·794	0·0602*	4·43	35·5
5·05	0·814	13·9	5·05	117·0
5·68	0·817	25·1	5·68	305·0
6·31	0·820	42·7	6·31	867·0
6·94	0·823	67·8	—	—
7·58	0·827	106·7	—	—

* Determined with Ostwald viscosimeter.

No quantitative theory can apply to the viscosity of emulsoids which does not take into account the fact that the tangential stress, expressed by the viscosity, must in part be expended in keeping the dispersed particles deformed against the forces due either to interfacial tension (liquid emulsions) or to the internal elasticity of the particles (dispersed gels); and in view of our ignorance of the shapes assumed by such particles under shear, the problem appears highly complex.

The authors' thanks are due to Mrs. B. Clemmow, B.Sc., and Miss D. S. Jones for their assistance; to the Director of Artillery for his permission to publish; to the Superintendent of Research, Woolwich, and to Sir Robert Robertson, F.R.S., for their interest in the work.

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OLD BLEACH LINEN CO., RANDALSTOWN. [*Received, March 5th*, 1920.]

XC.—*The Electrical Conductivity of Pure Salts in the Solid and Fused States. Determination of the Activity-coefficients of Ions in Solid Salts.*

By JNANENDRA CHANDRA GHOSH.

RECENT researches on *X*-ray analysis of crystal structure have proved conclusively that the atoms of a salt are arranged symmetrically in a space-lattice. Debye and Scherrer have also considered the possibility of ionisation in crystals of electrolytes (*Physikal. Zeitsch.*, 1918, **19**, 474). They assume that the diffract-

ing power of an atom depends on the number of electrons in the atom. This is equal to the Moseley number in a neutral atom. From the effective reflecting values of planes alternately wholly lithium and wholly fluorine, in a crystal of lithium fluoride, they conclude that the lithium atom has lost, and the fluorine atom has gained, an electron. Thus the internal ionisation of a solid salt is always complete.

Although ionisation is complete, the ions are not free to glide past one another, because of the great magnitude of the forces of cohesion, which prevent the displacement of an ion from its position of equilibrium in the crystal lattice. It is only at high temperatures, when the average kinetic energy of the ions has become sufficiently great for some of them to overcome this field of elastic force, that the electrical conductivity of the solid salt is observed. The number of free ions in a uni-univalent salt is given by the equation

$$2n = 2N \cdot e^{-\frac{W}{2RT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N is Avogadro's number and W may be defined as the work that the ions of a gram-molecule must perform against the forces of elasticity before they can be free to glide past one another at the absolute temperature, T. On the assumption that Ohm's law is always valid, the specific conductivity is given by the equation

$$\mu = \frac{2n}{v} \cdot U \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where v is the molecular volume of the salt and U the average mobility of the ions at T, or

$$\mu = \frac{U}{v} 2Ne^{-\frac{W}{2RT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Variation of W *with Temperature.*

The transition of ions from the bound to the free state inside the solid salt may be considered as a physico-chemical process attended with an absorption of energy, W, for each gram-molecule. In a condensed system, the variation of the energy of transition with temperature is given by the equation

$$W = W_0 + \beta T^2 \quad . \quad . \text{ Nernst theorem} \quad (4)$$

It appears plausible that equation (4) may be valid in this particular case. The nature of the forces operating in the interior of a solid salt is practically unknown, and can only be considered in a general way. Larmor has investigated the case of a fluid

composed of finite particles, and concludes that the force at an internal point, due to particles surrounding the point, is separable into two parts, one being due to the medium as a whole and the other a purely local part. The first part can be determined, as it depends on the potential due to the combined volume and surface-density distributions of Poisson. For an isotropic liquid, the second part can be easily neglected, as the particles are in a state of violent, irregular motion, and their axes are distributed quite haphazardly. In the case of a crystal, however, there is a definite geometrical configuration. The atoms, arranged in a space-lattice, immediately surrounding the point, give rise to a purely local force at that point. So long as the crystalline structure is maintained, the motion of the particles is not random, and there is no cancelling out of the forces due to each particle. The magnitude of W depends on the purely local part of the forces at an internal point, and from its very nature remains unknown. It is fairly certain, however, that it runs parallel with the forces of elastic rigidity inside a solid. It is well known that the plasticity of crystalline substances increases very rapidly with temperature, hence W diminishes with increasing temperature. β has thus a negative sign. At the melting point, where the purely local part of the forces is negligibly small, we may assume that

$$W = W_0 + \beta T_m^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where T_m is the melting point of the salt.

β can thus be easily expressed in terms of W_0 being equal to

$$-\frac{W_0}{T_m^2}.$$

Therefore at any temperature, T,

$$W = W_0 - \frac{W_0 T^2}{T_m^2} = W_0\left\{1 - \frac{T^2}{T_m^2}\right\} \quad . \quad . \quad . \quad (6)$$

Variation of the Mobility of the Ion of a Solid Salt with Temperature.

The variation of the mobility of an ion in a solid with rise in temperature can be easily accounted for in a way analogous to that developed in the electron theory of metallic conduction. If X is the strength of the electric field, the force acting on an ion is Xe. If the ion were perfectly free to move, there would be a constant acceleration of $\frac{Xe}{m}$ in the direction of the field, where m is the mass of the ion. There are, however, frequent collisions

with other ions, when all the accumulated energy of the ion is lost. It may be considered as the criterion of the solid state that the whole of the velocity of the free ion, added by the electric field, is removed at each collision, and the ion starts its course again with zero velocity. Let τ be the time taken by the ion to describe the mean free path, L. The velocity of the ion at the end of the mean free path due to the electrical field is $\frac{Xe\tau}{m}$. Therefore the average velocity added by the field in its own direction:

$$U' = \frac{1}{2} \cdot \frac{Xe\tau}{m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If V is the speed of the ion due to the combined effect of the electrical field and thermal agitation, then $\tau = \frac{L}{V}$. Since, however, the velocity of thermal agitation is very large compared with the velocity added by the electrical field, the value of V will be almost equal to V', the velocity due to thermal agitation alone. Therefore

$$U' = \frac{1}{2} \cdot \frac{Xe}{m} \cdot \frac{L}{V'}$$

$$V' = \sqrt{\frac{3 \cdot RT}{M}}$$

so that

$$U' = \frac{1}{2} \cdot \frac{e}{m} \cdot \frac{L}{\sqrt{3 \cdot R \cdot \frac{1}{M} \cdot T}} \cdot X \quad . \quad . \quad . \quad . \quad (8)$$

Now $L = \frac{\lambda^3}{\frac{4}{3}\pi S^2}$, where λ is the mean distance of the supposedly spherical ions and S the distance between the centres of gravity of two ions in collision. Since the coefficient of cubical expansion is negligibly small, L may always be regarded as constant.

Hence $$U' = \frac{k'}{\sqrt{T}} \cdot X$$

or the mobility

$$U = \frac{k'}{\sqrt{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Variation of the Specific Conductivity of a Solid Salt with Temperature.

Substituting the values of U and W from equations (9) and (6) respectively, in equation (3) we get

$$\mu = \frac{k'}{v} \cdot \frac{1}{\sqrt{T}} \cdot 2N \cdot e^{-W_0\left\{1 - \frac{T^2}{T_m^2}\right\}/2RT} \quad . \quad . \quad . \quad (10)$$

Since the change in molecular volume with temperature is negligible in the case of a solid,

$$\mu = \frac{k}{\sqrt{T}} \cdot 2N \cdot e^{-W_0\left\{1 - \frac{T^2}{T_m^2}\right\}/2RT}$$

or
$$\frac{W_0\left\{1 - \frac{T^2}{T_m^2}\right\}}{2RT} = \log_e^{2N \cdot K/\mu\sqrt{T}} \quad . \quad . \quad . \quad (11)$$

or
$$\frac{W_0(T_2 - T_1)}{2R}\left\{\frac{1}{T_1 T_2} - \frac{1}{T_m^2}\right\} = \log_e \frac{\mu_2\sqrt{T_0}}{\mu_1\sqrt{T_1}} \quad . \quad . \quad (12)$$

Equation (12) contains only one unknown constant, W_0, which can be easily obtained from any two values of μ. In the following tables, it will be seen how satisfactorily the above equation reproduces the observed values of μ. Column 4 of these tables contains the values of α—the activity-coefficient of the ions of a solid salt at various temperatures. They are calculated from equation (1):

$$\frac{W}{2RT} = \log_e \frac{2N}{2n} = \log_e \frac{1}{a} \quad . \quad . \quad . \quad . \quad (13)$$

or
$$\frac{W_0\left\{1 - \frac{T^2}{T_m^2}\right\}}{2RT} = \log_e \frac{1}{a} .$$

It will be noticed that the specific conductivity of the salts in some cases has increased almost a thousand times, but throughout this range, values of μ calculated from equation (12) agree with the observed values within 5 per cent. The observed specific conductivities in the case of sodium and potassium chlorides are taken from the work of Benrath and Wainoff (*Zeitsch. physikal. Chem.*, 1911, **77**, 257). The limits of experimental error, according to their own statement, are ±10 per cent. The data for the haloids of silver and thallium are obtained from the work of Tubandt and Lorenz (*Zeitsch. physikal. Chem.*, 1914, **87**, 529).

TABLE I.

Sodium Chloride.

$W_0 = 51{\cdot}2$ kg. cal. $T_m = 1083$ absolute.

T (absolute).	μ calc. $\times 10^6$.	μ obs. $\times 10^6$.	α calc.
903	—	12·6	0·0127
923	21·2	21·2	0·0216
943	35·4	35·0	0·0363
983	91·0	95·0	0·0988
1023	240·0	240·0	0·2551
1073	729·0	729·0	0·8034

TABLE II.

Potassium Chloride.

$W_0 = 50{\cdot}9$ kg. cal. $T_m = 1063$.

T.	μ calc. $\times 10^6$.	μ obs. $\times 10^6$.	α calc.
923	—	6·5	0·0324
933	8·4	8·4	0·0423
983	29·2	28·8	0·1469
1013	59·6	59·6	0·3095
1043	120·0	133·0	0·6295

TABLE III.

Silver Chloride.

$W_0 = 25{\cdot}6$ kg. cal. $T_m = 726$.

T.	μ calc.	μ obs.	α calc.
523	—	0·0003	0·0026
573	0·0016	0·0015	0·0142
623	0·0068	0·0065	0·0645
673	0·0260	0·0260	0·2587
723	0·0980	0·1100	0·9292

TABLE IV.

Silver Bromide.

$W_0 = 24{\cdot}8$ kg. cal. $T_m = 690$.

T.	μ calc.	μ obs.	α calc.
473	—	0·00052	0·00089
513	0·00238	0·00230	0·00427
553	0·01000	0·00910	0·01734
623	0·08000	0·08000	0·15600
673	0·36600	0·38000	0·63720

TABLE V.

Thallous Chloride.

$W_0 = 23{\cdot}75$ kg. cal. $T_m = 700$.

T.	μ calc.	μ obs.	α calc.
523	—	0·00005	0·00625
573	0·00024	0·00024	0·03162
623	0·00098	0·00090	0·23310
673	0·00360	0·00370	0·50870
694	0·00600	0·00610	0·86140

TABLE VI.

Thallous Bromide.

$W_0 = 21{\cdot}67$ kg. cal. $T_m = 730$.

T.	μ calc.	μ obs.	α calc.
523	—	0·00004	0·00612
623	0·00055	0·00055	0·09204
673	0·00170	0·00160	0·29510
720	0·00440	0·00470	0·81280

TABLE VII.

Thallous Iodide.

$W_0 = 18{\cdot}7$ kg. cal. $T_m = 710$.

T.	μ calc.	μ obs.	α calc.
523	—	0·0001	0·0160
623	0·0010	0·0010	0·1747
673	0·0027	0·0027	0·4898
702	0·0046	0·0048	0·8567

Electrical Conductivity of Fused Salts.

It follows from equation (6) that at the melting point all the ions are free to glide past one another, since W is zero at this temperature. Indeed, the belief is held generally that the activity-coefficient of fused salts is always unity. Thus, on considerations based on the molecular kinetic theory of Einstein, Lorenz draws the conclusion that fused salts are completely split up into free-moving ions ("Nernst Festschrift," p. 226. Halle, 1912). In the case of univalent molten salts, Arndt (*Zeitsch. Elektrochem.*, 1907, **13**, 510, 809) drew the same conclusion on the basis of investigations relating the viscosity with the molecular conductivity of the fused salt. Thus the specific conductivity of fused salts does not vary with temperature in a logarithmic way. This is to be expected, as all the ions present contribute to the conduction of electricity. As a general rule, the equation

$$\mu_2 = \mu_1\{1 - a(t_2 - t_1)\} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

is found to express satisfactorily the variation of conductivity with temperature, indicating that it is a simple case of variation of the mobility of the ion.

My best thanks are due to Prof. F. G. Donnan, F.R.S., for his suggestions and kind interest, and also to my friend, Mr. J. N. Mukherjee.

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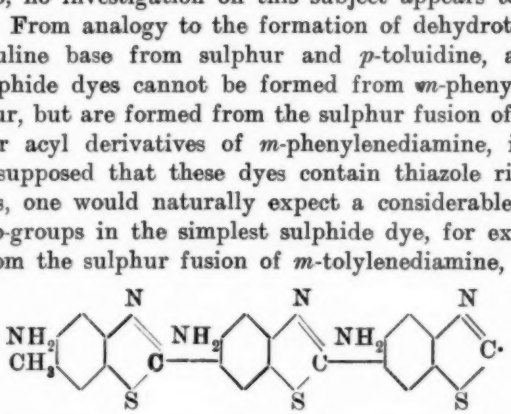
XCI.—*The Constitution of Yellow Sulphide Dyes.*

By JATINDRA KUMAR MAZUMDER and EDWIN ROY WATSON.

THE following experimental work is recorded as the authors will have no further opportunity for joint work on this subject. Unfortunately, the results obtained are as yet insufficient to allow of deductions as to the constitution of these dyes.

Hitherto, no investigation on this subject appears to have been recorded. From analogy to the formation of dehydrothiotoluidine and primuline base from sulphur and *p*-toluidine, and because yellow sulphide dyes cannot be formed from *m*-phenylenediamine and sulphur, but are formed from the sulphur fusion of *m*-tolylenediamine or acyl derivatives of *m*-phenylenediamine, it has been generally supposed that these dyes contain thiazole rings. From these ideas, one would naturally expect a considerable number of free amino-groups in the simplest sulphide dye, for example, that formed from the sulphur fusion of *m*-tolylenediamine,



One of us found, however, that the reaction of yellow sulphide dyes with nitrous acid, either in concentrated sulphuric acid solution or freshly precipitated and in aqueous suspension, is inappreciable, and this observation led to the present investigation.

Preparation and Analysis of the Dye.

Attempts to prepare what one would suppose to be the simplest yellow sulphide dye by the fusion of *m*-tolylenediamine and

sulphur according to D.R.-P. 139430 and 141576 gave a product with poor tinctorial properties, but a good yellow dye was obtained from the diformyl derivative of *m*-tolylenediamine by sulphur fusion according to D.R.-P. 138839, and this was used for the present investigation. The fusion product was extracted with carbon disulphide, dissolved in hot dilute sodium hydroxide solution, precipitated by hydrochloric acid, collected, washed, dried, and again extracted with carbon disulphide (Found: C*=41·5, 41·6, 41·4; H=3·2, 2·7, 2·5; N=9·5, 13·4, 11·0,† 11·7†; S=42·3, 44·6, 42·8).

Nitrogen was evolved very slowly in the estimation by Dumas's method, and the results were consequently untrustworthy. The figures obtained by Kjeldahl's method may be taken to indicate the lowest possible value of the percentage of nitrogen.

Another sample was exhaustively extracted with carbon disulphide, but was not dissolved in alkali and reprecipitated. These steps were omitted in order to avoid the introduction of impurities, as it was found that the reprecipitated substance filtered with difficulty and could not be easily washed (Found: C=42·9; H=2·98; S=42·3).

These figures indicate that the substance contains no oxygen. The proportion of carbon to nitrogen is less than in diformyl-*m*-tolylenediamine, $C_9H_{10}O_2N_2$, but greater than in *m*-tolylenediamine, $C_7H_{10}N_2$. $[(C_{17}H_{14}N_4S_{6\cdot27})_n$ requires C=42·98; H=2·95; N=11·8; S=42·27 per cent.]

On account of the tendency of sulphur to form polysulphide chains with any number of sulphur atoms, such a formula probably expresses the composition more correctly than one containing an integral number of sulphur atoms, but agreeing less closely with the analytical results.

*Experiments on the Formation of Dye with varying Proportions of Diformyl-*m*-tolylenediamine and Sulphur.*

The mixture was in each case heated according to D.R.-P. 138839. The products were finely powdered and washed in succession with carbon disulphide and water.

Expt. (1).—Two parts of diformyl compound and 4 parts of sulphur gave 3 parts of dye.

Expt. (2).—Two parts of diformyl compound and 2 parts of sulphur gave 1·9 parts of dye.

* C, H, and S determined together by Dennstedt's method.
† By Kjeldahl's method.

Expt. (3).—Two parts of diformyl compound and 1 part of sulphur gave 1·05 parts of dye.

In Expt. (1), the proportions are those specified in the patent. The product from Expt. (2) was an equally strong dye, but that from (3) was much weaker.

Lead Salt.—On adding a solution of lead acetate to a solution of the dye in dilute sodium hydroxide, there was obtained a brown precipitate. This filtered very badly, but was washed first by decantation. (Found: Pb=51·0, 51·1. $C_{17}H_{10}N_4S_{6\cdot27}Pb_2$ requires Pb=46·8 per cent.).

This result seems to indicate that there are approximately two mercaptan or acidic groups for each molecule of diformyl-*m*-tolylenediamine which has entered into the formation of the dye.

Oxidation of the Dye in Alkaline Solution with Potassium Permanganate.

One gram of the dye was dissolved in a solution of 2·5 grams of potassium hydroxide in 20 c.c. of water, and a solution of 2·5 grams of potassium permanganate in 50 c.c. of water was gradually added while the mixture was kept cool. The permanganate was immediately destroyed. The mixture was boiled and filtered hot, and the residual manganese dioxide was extracted with boiling water. On concentrating the filtrate and washings to 25 c.c. and acidifying with hydrochloric acid, sulphur dioxide was evolved, and a red precipitate was obtained, which was collected. Nothing was extracted from the filtrate by shaking with ether. The precipitate was washed with cold water and dried, first on a tile and then in an air-oven at 120° (analysis No. 1). It is somewhat soluble in cold, and almost completely so in hot, water. With the idea of preparing a purer sample for analysis, the precipitate from another preparation was boiled with excess of water and filtered hot, the filtrate was evaporated to dryness, and the residue dried in the air-oven for analysis (No. 2). This gave, however, a large quantity of ash, so it was washed with dilute hydrochloric acid and again dried and analysed (No. 3).

(1) C=42·5; H=3·57; S=29·2.
(2) C=41·7; H=4·5; S=32·1.
(3) C=42·1; H=3·1; S=24·9; N=11·7.

The samples contained 4·25 and 4·3 per cent. of ash respectively. The percentages are reckoned on ash-free substance.

$C_9H_8O_3N_2S_2$ requires C=42·2; H=3·1; N=10·9; S=25·0.
$C_{17}H_{14}O_5N_4S_{3\cdot69}$ requires C=43·2; H=2·96; N=11·8; S=25·0 per cent.

The latter formula is preferred because it contains the same number of carbon, hydrogen, and nitrogen atoms as the original dye. On the most natural assumption that this substance is a sulphonic acid, we require a complex of at least $(C_{17}H_{14}N_4S_{6\cdot27})_6$ in the dye to explain its formation, which is represented as follows:

$$(C_{17}H_{12}N_4S_2)_6(S\cdot SH)_5(S\cdot S\cdot SH)_5 \longrightarrow (C_{17}H_{12}N_4S_2)_6(SO_3H)_{10}.$$

We deduce from this that the dye complex formed from twelve molecules of diformyl-*m*-tolylenediamine contains five ·S·SH groups and five ·S·S·SH groups, which are all converted into sulphonic acid groups on oxidation. There only remain twelve sulphur atoms for ring-formation, that is, one atom for each molecule of diformyl-*m*-tolylenediamine. According to this, only half the nitrogen can be involved in thiazole rings.

These conclusions are apparently opposed to those deduced from the analysis of the lead salt of the dyes, from which we inferred the presence of approximately two mercaptan or acidic groups for each molecule of diformyl-*m*-tolylenediamine concerned in the formation of the dye. It is just conceivable, however, that other atoms or groups, for example, a nitrogen atom in the ring, may exhibit acid properties.

Bases formed by the Action of Hydriodic Acid and Red Phosphorus on the Dye.

On boiling with these reagents under reflux, there is at first a little evolution of hydrogen sulphide, but, after many hours' boiling, the dye is apparently unchanged. Two and a-half grams were boiled for six hours with 0·8 gram of red phosphorus and 15 c.c. of hydriodic acid (D 1·7). The mixture was then transferred to a thick-walled glass tube, a further 0·8 gram of red phosphorus and 10 c.c. of hydriodic acid were added, the tube was sealed, and heated at 190—213° for eight and a-half hours. Much hydrogen sulphide was produced. The bulk of the hydriodic acid was distilled off, and the residue was distilled with water and filtered. On adding sodium acetate to the filtrate, a bright yellow, flocculent precipitate was formed, which was collected, washed, and dried (base *A*). On adding sodium carbonate to the filtrate and extracting repeatedly with ether, a dark brown, tarry substance was obtained (base *B*). The amount of *A* was about 0·25 gram and of *B* about 0·5 gram.

Base A.—After drying on a porous tile, this melted and decomposed at 180—200°. No crystalline acetyl derivative could be obtained from it. (Found: C=58·5; H=5·6; N=13·96; S=12·2.

$C_{38}H_{44}O_5N_8S_3$ requires C=57·9; H=5·59; N=14·2; S=12·2 per cent.).

Base B.—On one occasion a few crystals were obtained by acetylating with acetic anhydride and pyridine, evaporating to dryness, and crystallising from alcohol. Attempts to obtain more crystals were, however, unsuccessful. This base contained no sulphur (and no iodine). [Found: C=61·9; H=7·37; N=8·4. M.W.=314 (determined by the cryoscopic method in glacial acetic acid solution). NH_2=4·16 (determined by dissolving in dilute hydrochloric acid and titrating with standard nitrite solution). $C_{17}H_{22}O_5N(NH_2)$ requires C=60·7; H=7·14; N=8·33; NH_2=4·76 per cent.].

By coupling the diazotised solution with β-naphthol in alkaline solution, a crimson dye was obtained, which was insoluble in dilute sodium hydroxide solution.

The presence of oxygen in these bases was unexpected. Their chemical behaviour seems inconsistent with the presence of hydroxyl or carboxyl groups. The substances were heated to constant weight at about 130° before analysis. However, if we assume the oxygen to be contained in molecularly attached water, the formulæ become $C_{38}H_{34}N_8S_3,5H_2O$ and $C_{17}H_{12}N(NH_2),5H_2O$. In a very approximate way, these formulæ may be interpreted as indicating that the polysulphide groups are first removed, and subsequently the cyclic sulphur is eliminated with half the nitrogen (one atom of nitrogen being removed with each atom of sulphur). As only half the remaining nitrogen is in the amino-form, the other half probably forms part of an unbroken ring connecting two benzene nuclei and not containing sulphur.

The action on the dye of tin and hydrochloric acid, zinc dust and sodium hydroxide, bromine, sodium hypobromite, phosphorus pentachloride, phosphorus pentachloride and phosphoryl chloride, phosphorus trichloride, or hot concentrated sulphuric acid has not given products which seem likely to assist in determining the constitution. Up to the present, nothing of interest has been obtained by the action of nitric acid.

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XCII.—*The Determination of the Relative Strengths of some Nitrogen Bases of the Aromatic Series and of some Alkaloids.*

By Francis Arnall.

In the selection of a method by which to determine the relative strengths of the bases of the aromatic series, it must be borne in mind that on the whole they are feeble bases, and, furthermore, that they are usually almost insoluble in water. On the other hand, the salts of these bases are soluble. The author therefore considered that the most satisfactory method would be to measure the degree of hydrolysis of the hydrochlorides in aqueous solution by observing the acceleration of the rate of inversion of a solution of sucrose by means of the polarimeter. In using this method, care must be taken to ensure the same constant temperature throughout all the experiments. Moreover, since the preparation of the hydrochlorides of many of the bases was not possible, the solutions had to be prepared by the addition of the requisite quantity of acid to the weighed base after careful purification of the latter.

In carrying out an experiment, equal volumes of the sucrose solution (5 grams per 100 c.c.) and the solution of the hydrochloride were brought to 55° in the thermostat, mixed, and rapidly transferred to a well-jacketed polarimeter tube, provided with false ends to check loss of heat by radiation, already maintained at the correct temperature. The first reading was taken as soon as the thermometer was steady, and readings were then made at intervals until the reaction was sufficiently advanced. The "final rotation," when the sugar was completely inverted, was read after the solution had been heated to 80° for fifteen minutes. The degree of hydrolysis of the hydrochloride was deduced from the velocity of reaction by comparison with the velocities of inversion by hydrochloric acid alone.

The degree of hydrolysis having been found at several dilutions, the dissociation constant of the salt, the basic constant of the base, and the relative strength of the base to aniline were calculated. As an example of the results obtained, the following may be given:

Salt.	Dilution = v.	Degree of hydrolysis = β at 55°.	Dissociation constant $K_s = \frac{\beta^2}{(1-\beta)V}$
Dimethylaniline hydrochloride.	4	0·0098	$2{\cdot}4 \times 10^{-5}$
	8	0·0133	$2{\cdot}3 \times 10^{-5}$
	16	0·0189	$2{\cdot}3 \times 10^{-5}$

A small excess of free hydrochloric acid in the solution of the hydrochloride sometimes improved the clarity of the solution, enabling more accurate readings to be taken, whilst its effect on the degree of hydrolysis was found to be negligible.

Usually, the excess of acid was not more than a small percentage of the acid set free by hydrolysis. For example, diphenylamine hydrochloride in $N/240$-solution was dissociated to the extent of 89 per cent.; the amount of free acid apart from this was $N/2400$. Thus the excess of acid was equal to 11 per cent. of the free acid due to the hydrolysis of the salt. In the case of stronger bases, where the degree of hydrolysis was small, the excess of acid used was of the same order as the free acid due to hydrolysis. Before accepting the results obtained in this way, experiments were carried out with quinoline hydrochloride in order to ensure that this did not invalidate the results.

Concentration of the hydrochloride.	Concentration of the excess acid.	Total free acid in solution.	Degree of hydrolysis. Per cent.
$N/4$	$N/200$	$N/98{\cdot}9$	2·045
$N/4$	$N/400$	$N/131{\cdot}2$	2·05

It will be seen that doubling the amount of excess acid did not affect the degree of hydrolysis.

In the case of dimethylaniline, consistent results were only obtained by the use of freshly prepared solutions of the base recently fractionated under diminished pressure, since the solution of the hydrochloride, although prepared with freshly distilled conductivity water and kept in the dark, changed in the course of a few hours to a pale heliotrope colour, even in well-stoppered bottles. Crystalline dimethylaniline hydrochloride could be prepared by passing pure dry hydrogen chloride into a dry ethereal solution of the base, but it was considered preferable to use the solution obtained by the addition of pure acid to the pure base.

The volatility of pyridine rendered the preparation of the hydrochloride solution inaccurate unless great care were taken.

The more common alkaloids, such as strychnine, brucine, cocaine, and morphine, were found to be too strongly basic to give satisfactory results by this method.

The velocity of inversion of the sucrose solution was, even with some of the solutions used, only sufficiently rapid for convenient measurement at the temperature employed, namely, 55°. It was established by experiment that coloration of the sugar solution sometimes occurred on prolonged warming at temperatures a little above 55°.

The following tables summarise briefly the results obtained.

Table I.

The Relative Strengths and Basic Constants of the Bases.

Base.	K_s.	$K_b = \frac{K_w}{K_s}$.	Aniline = 100.
Dimethylaniline	$2{\cdot}3 \times 10^{-5}$	$5{\cdot}22 \times 10^{-10}$	430·0
p-Toluidine	$4{\cdot}0 \times 10^{-5}$	$3{\cdot}00 \times 10^{-10}$	250·0
m-Xylidine	$8{\cdot}5 \times 10^{-5}$	$1{\cdot}41 \times 10^{-10}$	120·0
Aniline	$1{\cdot}00 \times 10^{-4}$	$1{\cdot}20 \times 10^{-10}$	100·0
Pyridine	$1{\cdot}01 \times 10^{-4}$	$1{\cdot}19 \times 10^{-10}$	99·0
Quinoline	$1{\cdot}07 \times 10^{-4}$	$1{\cdot}12 \times 10^{-10}$	93·0
o-Toluidine	$1{\cdot}59 \times 10^{-4}$	$7{\cdot}50 \times 10^{-11}$	62·0
m-Aminobenzoic acid	$8{\cdot}7 \times 10^{-4}$	$1{\cdot}38 \times 10^{-11}$	11·0
p-Aminobenzoic acid	$9{\cdot}5 \times 10^{-3}$	$1{\cdot}26 \times 10^{-12}$	1·1
o-Aminobenzoic acid	$1{\cdot}63 \times 10^{-2}$	$7{\cdot}36 \times 10^{-13}$	0·61
Diphenylamine	$2{\cdot}9 \times 10^{-2}$	$4{\cdot}14 \times 10^{-13}$	0·34
Aceto-*p*-toluidide	$3{\cdot}2 \times 10^{-2}$	$3{\cdot}75 \times 10^{-13}$	0·31
Benzo-*p*-toluidide	$4{\cdot}0 \times 10^{-2}$	$3{\cdot}00 \times 10^{-13}$	0·25
Aceto-*m*-4-xylidide	$4{\cdot}5 \times 10^{-2}$	$2{\cdot}67 \times 10^{-13}$	0·22
Acetanilide	$4{\cdot}8 \times 10^{-2}$	$2{\cdot}50 \times 10^{-13}$	0·21
Aceto-*o*-toluidide	$5{\cdot}3 \times 10^{-2}$	$2{\cdot}26 \times 10^{-13}$	0·19
Benzo-*m*-4-xylidide	$5{\cdot}3 \times 10^{-2}$	$2{\cdot}26 \times 10^{-13}$	0·19
Benzanilide	$5{\cdot}5 \times 10^{-2}$	$2{\cdot}18 \times 10^{-13}$	0·18
Benzo-*o*-toluidide	$5{\cdot}9 \times 10^{-2}$	$2{\cdot}03 \times 10^{-13}$	0·17

K_s = hydrolysis constant of the hydrochloride in aqueous solution.

K_b = basic constant.

K_w = dissociation constant for water, assumed to be equal to $1{\cdot}2 \times 10^{-14}$ for 55°.

Table II.

Relative Strengths and Basic Constants of Alkaloids.

Alkaloid.	K_s.	$K_b = \frac{K_w}{K_s}$.	Aniline = 100.
Quinine	$5{\cdot}1 \times 10^{-6}$	$2{\cdot}35 \times 10^{-9}$	2000·0
Narcotine	$4{\cdot}2 \times 10^{-5}$	$2{\cdot}86 \times 10^{-10}$	240·0
Cinchonine	$6{\cdot}1 \times 10^{-5}$	$1{\cdot}97 \times 10^{-10}$	160·0
Quinidine	$7{\cdot}5 \times 10^{-5}$	$1{\cdot}60 \times 10^{-10}$	130·0
Piperine	$3{\cdot}8 \times 10^{-2}$	$3{\cdot}16 \times 10^{-13}$	0·26
Caffeine	$6{\cdot}0 \times 10^{-2}$	$2{\cdot}00 \times 10^{-13}$	0·17
Theobromine	$8{\cdot}3 \times 10^{-2}$	$1{\cdot}45 \times 10^{-13}$	0·12

Table III.

Decrease in Basic Strength on forming Acetyl and Benzoyl Derivatives.

Base.	Strength of base.	Strength of acetyl derivative.	Strength of benzoyl derivative.
p-Toluidine	250	0·31	0·25
m-4-Xylidine	120	0·22	0·19
Aniline	100	0·21	0·18
o-Toluidine	62	0·19	0·17

All the values given are relative to aniline = 100.

As would be expected, the benzoyl derivatives are weaker than the corresponding acetyl derivatives, and the order of strength of the bases is also the order of strength of their acyl derivatives.

TABLE IV.

Percentage Degree of Hydrolysis of Hydrochlorides of Bases.

A.

Base.	$v=100$.	$v=150$.	$v=200$.
Acetanilide	—	89·0	91·2
Aceto-*o*-toluidide	—	90·0	92·0
Aceto-*p*-toluidide	—	84·9	87·9
Aceto-*m*-4-xylidide	—	88·2	90·8
Benzanilide	—	90·2	92·4
Benzo-*o*-toluidide	—	90·6	92·7
Benzo-*p*-toluidide	—	87·3	90·0
Benzo-*m*-4-xylidide	—	89·7	92·0
Caffeine	87·5	90·8	—
Narcotine	6·3	—	—
Piperine	82·5	86·4	—
Theobromine	90·3	93·0	—

B.

Base.	$v=4$.	$v=8$.	$v=16$.
Aniline	1·98	—	3·92
Dimethylaniline	0·98	1·33	1·89
Pyridine	1·99	—	3·95
Quinine	—	0·64	—
Quinoline	2·05	—	4·12
o-Toluidine	2·50	—	4·90
p-Toluidine	1·25	—	2·49
m-4-Xylidine	—	2·58	3·61

C.

Base.	$v=32$.	$v=40$.	$v=64$.	$v=80$.	$v=160$.	$v=240$.
m-Aminobenzoic acid.	15·4	—	20·9	—	—	—
o-Aminobenzoic acid	—	54·6	—	66·3	—	—
p-Aminobenzoic acid	—	—	—	57·3	68·8	—
Diphenylamine	—	—	—	—	84·7	88·7

D.

Base.	$v=10$.	$v=15$.	$v=20$.	$v=30$.
Cinchonine	2·44	3·00	—	—
Narcotine	—	—	2·9	—
Quinidine	—	—	3·8	4·6
Quinine	0·71	—	—	—

Conclusions.—(*a*) The method employed is suitable for the determination of the strengths of the bases of the aromatic series and of similarly weak bases, and gives consistent results if care be taken.

(*b*) The method is applicable only to the more feebly basic alkaloids; for the stronger alkaloids, such as strychnine and cocaine, other methods should be adopted.

The author desires to acknowledge his indebtedness to the Principal and to the Head of the Chemical Department in permitting him to carry on this work.

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XCIII.—*The Transition from Coal to Coke.*

By ERIC SINKINSON.

COKE is a conductor of electricity, but it can easily be demonstrated that coal is not. It was with a view to determine whether, during the carbonisation of coal, the change from a non-conducting to a conducting condition is gradual or abrupt, that the experiments recorded in this paper were undertaken. It seems probable that the change is one in which free carbon liberated by the thermal decomposition of the coal forms an electrically conducting bridge in the non-conducting medium. Two conditions at least are necessary before this can take place: (*a*) that a minimum quantity of coke must be formed; (*b*) that the particles of free carbon forming the coke must be in a fine state of division. Consider the case where all the particles are spherical; then if in a state of maximum coarseness, where all the particles are combined into one large one, evidently there cannot be a bridge across the non-conducting medium, but if the conglomerate is finely ground, the particles will touch and form a bridge. Beyond a certain degree of fineness, the size of the particles should not affect the conductance. It seems reasonable to assume that carbon formed by heating coal will be in such a state as required by (*b*).

EXPERIMENTAL.

A.

Before attempting to measure the electrical resistance of carbonised coal, it was decided to find how coke itself in a fine state of division would behave when evenly distributed in a non-

conducting medium, such as pitch. Accordingly, two cokes were selected, namely, a Durham (Langley Park) and one from a Welsh bituminous coal of an upper seam in the lower coal measures. The coke was ground in a mill until it would pass a mesh of 200 to the linear inch (80 to the cm.), and dried at 105° in the ordinary way. It was then intimately mixed with 10 per cent. of pitch. The mixture was transferred to a stout cylinder of steel of 2·5 cm. cross-section, fitted with plungers top and bottom, and the whole placed in a hydraulic press, where the contents of the cylinder were subjected to a pressure of 31·5 kilos. per sq. mm. until they did not yield. In this manner, a series of briquettes was prepared with increments of 10 per cent. of pitch, until the last one reached 90 per cent.

The briquettes were prepared for the measurement of their electrical resistances in the following manner. Two holes were drilled from the top 1 cm. apart and 2 cm. deep. These were filled with mercury to establish good contact with the wires connected to the measuring instrument. This consisted of the well-known post-office box form of the Wheatstone bridge arranged with a cell and galvanometer in the circuit. A d'Arsonval mirror type of galvanometer was employed. If the resistance of the briquette was beyond the compass of the bridge, it was placed in circuit with the galvanometer and cell, and the deflexion compared with that obtained by a resistance of known magnitude. The resistances were measured in ohms, the reciprocals of which have been tabulated as conductances (mhos.) for convenience.

TABLE I.

Durham coke, per cent.	Pitch, per cent.	Resistance, ohms.	Conductance, mhos.
100	—	0·16	6·20
90	10	0·64	1·85
70	30	0·90	1·11
50	50	5·65	0·17
30	70	71·00	0·014
20	80	20,500·00	5×10^{-5}
10	90	> 500,000·00	$< 10^{-6}$
Welsh coke, per cent.			
100	—	0·20	5·0
90	10	0·75	1·33
70	30	0·87	1·15
50	50	6·40	0·15
30	70	60·00	0·016
20	80	22,000·00	$4·6 \times 10^{-5}$
10	90	> 500,000·00	$< 10^{-6}$

It is evident that more than 10 per cent. of free carbon must be present in a non-conducting medium to form an electrically conducting bridge.

B.

In order to find out what is the minimum temperature at which coal must be heated before it will conduct electricity, it was decided for experimental convenience to reverse the order and prepare a series of cokes from the same coal, carbonised every 100° below 900°, and measure the electrical resistance of each. To do this, the coal was pulverised and placed in a silica tube closed at one end to form a retort, the open end being closed by a rubber stopper carrying a delivery tube. The delivery tube was connected with an aspirator filled with a mixture of glycerol and water; a manometer was inserted to indicate the slightly diminished pressure maintained throughout carbonisation. The distillation tube and connexions were exhausted, and heat was applied by an electric muffle, the temperature of which was measured by a platinum-rhodium–platinum thermocouple. The first experiment was made at 900°, and lasted two hours.

Similar experiments were made at 800°, 700°, 600°, 500° and 400°, the last three being in glass tubes.

The cokes were removed in turn from the tubes, and powdered in a mill until they would pass a mesh of 200 to the inch (80 to the cm.). Each was briquetted at 31·5 kilos. per sq. mm., those carbonised at 900° down to 700° requiring 10 per cent. of pitch to bind them. As, however, the effect of 10 per cent. of pitch on the resistance of the coke is known from the earlier experiments, this addition can be allowed for in comparing results. The cokes carbonised below 700°, however, were self-binding under the above treatment. The briquettes were prepared for the measurement of their electrical resistance in the same way as before.

The coals employed were Durham and Welsh, and the results obtained are as follows:

TABLE II.

C.

Temperature of Durham.			Temperature of Welsh.		
Carbonisation.	Ohms.	Mhos.	Carbonisation.	Ohms.	Mhos.
900°	0·13	7·7	900°	0·20	5·0
800	0·60	1·7	800	0·75	1·3
700	100·0	0·01	700	140·00	0·006
600	4,300	2×10^{-4}	600	6,000	$1{\cdot}7\times10^{-4}$
550	7,900	$1{\cdot}2\times10^{-4}$	550	40,000	2×10^{-5}
500	$>500{,}000$	$<10^{-6}$	500	$>500{,}000$	$<10^{-6}$
400	$>500{,}000$	$<10^{-6}$	400	$>500{,}000$	$<10^{-6}$

The resistance of the briquettes became too great to measure below a carbonising temperature of 550°. By comparing the results of table I with those of II, it is evident that for a carbonising temperature of 550°, between 10 and 20 per cent. of free carbon is liberated from the coal. The critical temperature of the formation of coke lies between 500° and 550°.

In order to determine more precisely the temperature at which this change takes place, and whether the conduction commences suddenly or gradually, the method of investigation was modifled in the following manner. A weighed quantity of approximately 15 grams of the dried and powdered coal under examination was introduced midway into a hard glass tube open at both ends, and in it were embedded two platinum wires 1 cm. apart, which extended beyond the open ends of the tube. The contents were held firmly in position by asbestos plugs. The tube was placed in an electric furnace, where its temperature could be raised over any desired range. The platinum wires leading from the carbonising tube were put in circuit with a battery and one of the galvanometers of the Darwin double thread recorder. A thermocouple to measure the temperature of the furnace was connected to the other galvanometer.

The purpose of this arrangement was to record simultaneously the temperature of the heated coal and the current it conducted, so that the temperature at which the coal would just conduct a current of electricity could be precisely determined. The record is registered automatically in the form of a series of dots made at intervals of a minute.

The first coal to be tried was the Welsh, used in the previous experiments. When the temperature reached 500°, the needle of the galvanometer in circuit with the coal moved from the zero position and plotted a series of ever-widening dots on the chart, thus indicating an increase in the conductance of the coal as the temperature rose above the critical value.

In this manner, critical conducting values were found for Durham, Spanish coking and non-coking coals of similar composition, a Silkstone coal, cellulose, Yacca gum resin, and starch, with the results shown in table III.

Records were also taken as the electric muffle cooled. The conductance broke down, however, on account of the contraction of mass, which consequently developed fissures.

The Spanish non-coking coal showed the lowest critical value of the series tested, namely, 450°, and the rest were from 500° to 530°. The value for cellulose was of the same order, namely, 500°.

TABLE III.

Substance.	Temperature at which conductance began.
Welsh	500°
Durham	530
Spanish coking	500
Spanish non-coking	450
Silkstone	500
Cellulose	500
Yacca resin	not below 640°
Starch	580°

Yacca gum resin remained non-conducting even at 640°. Although the resin appeared to have carbonised, it formed such a loose, cellular mass that no contact was set up between the ends of the platinum wires embedded in it.

Discussion of Results.

It is evident from the results of the foregoing experiments that coal under the influence of heat begins to yield free carbon at a temperature in the region of 500°. Below this temperature, decomposition has been proceeding, but not true "carbonisation" in the sense of the formation of free carbon. The critical change in the conduction at this temperature indicates that true carbonisation has begun. Since the same effect is produced with cellulose, it appears probable that the formation of free carbon at this temperature is due to the decomposition of the cellulosic constituents of the coal.

It was found by the author (this vol., p. 166) that coals carbonised about 500° gradually lost the power of producing an image on a photographic plate in the dark. It would appear that decomposition of the coal begins at 450° and continues to 500°, at which temperature sufficient free carbon has been liberated to form a conducting bridge in the coal. At this stage, there will be present not less than 10 per cent. of free carbon. It may be concluded that on carbonising coal, there is sharp transition to coke after a certain limiting temperature has been reached, evidenced by the rapid increase in its conductance above this temperature.

The author wishes to record his best thanks to Prof. W. A. Bone for his interest in the work.

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LONDON. [*Received, May 31st*, 1920.]

XCIV.—*Periodic Precipitation. Part I. Silver Chromate in Gelatin.*

By Alexander Mitchell Williams and Mary Russell MacKenzie.

The object of this research was to examine the influence of the different factors affecting periodic precipitation in gels. The presence of a gel would not appear to be absolutely essential for the formation of a periodic precipitate in some cases, as is shown by Dreaper (*Kolloid Zeitsch.*, 1914, **14**, 163), amongst others, but in the majority of examples studied a gel has been present. The best known case is probably that of silver chromate in gelatin, discovered by Liesegang, after whom the phenomenon is usually named, although the first investigator appears to have been Runge (Leduc, "Mechanism of Life," p. 67. See Rayleigh, *Phil. Mag.*, 1919, [vi], **38**, 738, and Bradford, *Biochem. J.*, 1920, **14**, 29). Liesegang found that the diffusion from a drop of silver nitrate solution placed on a gelatin film impregnated with potassium dichromate produced a precipitate, not continuously, but in rings—Liesegang's rings. If the reaction takes place in a test-tube, layers of precipitate are produced.

In a summary of recent work on the subject, E. Hatschek ("Second Report on Colloid Chemistry," *Rep. Brit. Assoc.*, 1919, 21) indicates the various theories advanced in explanation. The earliest, due to Ostwald, assumes supersaturation, followed by precipitation, and consequent clearing of the immediate neighbourhood of the precipitate from the reactants, so that the diffusing ion has to travel some distance before precipitation again occurs. Hatschek holds that this theory is disproved by the fact that periodic precipitation still takes place in the presence of crystalline nuclei of the precipitate or of a previous stratification which should have rendered supersaturation impossible. No allowance is here made for the slowness of a reaction in a viscous medium, and it is assumed that equilibrium exists between the crystals and the substance to be precipitated. Barger and Field (T., 1912, **101**, 1397, and private communication from Prof. Barger), however, found that a "supersaturated" solution of saponarin was colloidal, and the substance did not crystallise on addition of crystals of saponarin. Another theory, due to Bradford, attributes the removal of the reactant before the precipitate to adsorption, a view which is discussed later. Other observers have emphasised the protective action of the emulsoid present as leading to something equivalent to

"supersaturation," and it was this influence that we first sought to study.

The material employed was Cox's best gelatin. A 0·5 per cent. solution of this set readily at the ordinary temperature. Analysis showed it to yield an ash of 1·2 per cent., consisting of calcium oxide with some calcium sulphate. When dried to constant weight at 105°, the loss was 17·6 per cent. All weights of gelatin are expressed in terms of the gelatin containing 17·6 per cent. of moisture, and volume concentrations are employed throughout. The reaction first studied was the production of silver chromate by the interaction of silver nitrate and potassium chromate (for literature, see Bradford, *loc. cit.*).

The following is an example of the method employed. Five c.c. of $N/400$-silver nitrate were placed in each of a row of test-tubes, and 5 c.c. of $N/400$-potassium chromate into each of another row. Then into each test-tube were put successively 2·5, 2·6, 2·7, . . . c.c. of 0·2 per cent. gelatin. The contents of corresponding test-tubes were now mixed, and the point was noted where the precipitate of silver chromate failed to appear, say at 2·7 c.c. of gelatin. It was now easy to calculate the concentration of the silver chromate and of the gelatin. Thus the gelatin concentration is evidently

$$\frac{2{\cdot}7}{5+2{\cdot}7} \times 0{\cdot}2 = \frac{0{\cdot}54}{7{\cdot}7} = 0{\cdot}070 \text{ per cent.}$$

whilst the normality of the silver chromate solution is

$$0{\cdot}5 \cdot \frac{5}{5+2{\cdot}7} \cdot \frac{N}{400} = \frac{10N}{7{\cdot}7 \times 1600} = 0{\cdot}00081N.$$

The weight of gelatin keeping a gram-equivalent of silver chromate in solution, ignoring the saturation concentration in water $0{\cdot}0002N$, is evidently

$$0{\cdot}070 \times 10/0{\cdot}00081 = 860 \text{ grams.}$$

It was soon found necessary to fix a maximum time for the appearance of the precipitate. This was arbitrarily selected as seventy-two hours. The test-tubes were immersed in a thermostat maintained at 25°, since leaving the solutions exposed to the ordinary temperature overnight led to discordant results. By a system of rigorous cleaning of the tubes by ammonia, hot water, and steaming, results were finally obtained reproducible within 0·2 c.c. of gelatin solution, this being the limit of accuracy attempted.

Observations were made on solutions containing up to 4·5 per cent. of gelatin. With the most concentrated solutions, precipitation usually started at the surface of the gel. This was most prob-

ably due to evaporation of water to the slightly cooler portion of the corked tube above the surface of the water in the thermostat. It did not seem likely from its appearance to be due merely to adsorption concentration on the surface. With the moderately concentrated gels, precipitation was usually general and very fine, although at other times it was more massive. With the solutions that did not set, there occurred an interval just at the limit of precipitation, where a very small trace of precipitate settled out and no more appeared. This was strikingly like the separation from a slightly supersaturated solution of the excess of solute. With the very dilute solutions, the precipitate which appeared was almost invariably in the form of extremely minute crystals at the bottom of the test-tube. Here the slowness with which a precipitate appeared, and its minuteness when it did appear, rendered observations somewhat difficult. Sometimes at any concentration a point would be found in a series of precipitates where no precipitate had appeared on keeping, and inoculation with a trace of precipitate did not induce immediate precipitation. Table I exemplifies the reproducibility of the results. Here a plus sign indicates presence of precipitate in quantity, a plus with an interrogation the trace of precipitate referred to, and a minus absence of precipitate after seventy-two hours.

TABLE I.

N/400-Silver nitrate and *N*/400-potassium chromate. 0·2 Per cent. gelatin.

C.c. gel.	Precipitate.	C.c. gel.	Precipitate.	C.c. gel.	Precipitate.
1·8	+	2·4	+	2·6	+?
2·0	+	2·6	+?	2·8	+?
2·2	+	2·8	−	3·0	−
2·4	+	3·0	−	...	...
2·6	+	3·2	−	...	...
2·8	−	3·4	−	...	...

The results of a series of such observations are presented in table II, where the first column gives the volume in litres of solution containing a gram-equivalent of silver nitrate and potassium chromate, and the last column the number of c.c. of gelatin solution added to 5 c.c. of the reacting solutions. From table II may be calculated, by the method already exemplified, the values given in table III, where the first column contains the normality of the silver chromate, the second the percentage concentration of the gelatin, and the last the weight, in grams, of gelatin preventing precipitation of a gram-equivalent of silver chromate.

TABLE II.

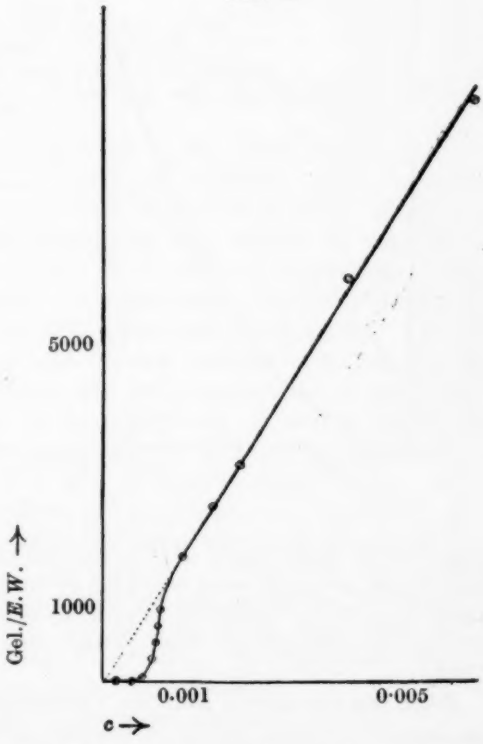
Volume.	Gelatin. Per cent.	C.c.
5000	0·0	0·0
1000	0·001	0·8
800	0·01	1·0
600	0·01	2·3
550	0·1	1·5
500	0·2	1·5
400	0·2	2·7
300	0·2	4·7
250	0·5	3·7
200	1·0	3·1
100	1·0	7·7
50	2·0	11·8
50	3·0	9·6
25	6·0	13·8

TABLE III.

Normality.	Gelatin. Per cent.	Gelatin. $\frac{}{E.W.}$
0·0002	0·0	0·0
0·00043	0·00014	3·2
0·00052	0·0017	32·0
0·00057	0·0031	55·0
0·00070	0·023	330·0
0·00077	0·046	600·0
0·00081	0·070	860·0
0·00086	0·097	1130·0
0·00115	0·20	1850·0
0·00154	0·38	2500·0
0·00197	0·61	3100·0
0·00297	1·40	4700·0
0·00345	1·96	5700·0
0·0053	4·4	8300·0

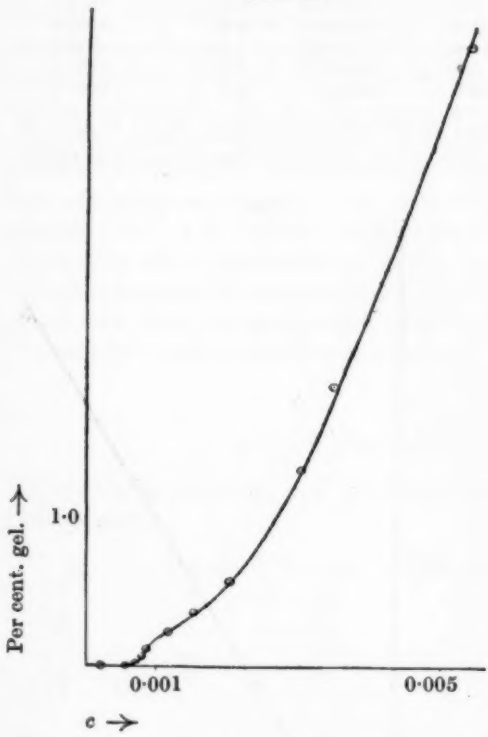
These results are presented in graphical form in Figs. 1 and 2. It will be seen from Fig. 1 that, so far as these observations extend, there is no indication of a limiting concentration of silver chromate above which gelatin will fail to prevent precipitation. Another remarkable feature is the smallness of the weight of gelatin preventing precipitation at the lowest concentration. We may compare this with the values calculated from Zsigmondy's gold numbers (*Zeitsch. anal. Chem.*, 1902, **40**, 697) for gelatin. Thus 10 c.c. of a gold sol containing 0·055 gram per litre were protected by 0·005—0·01 milligram of gelatin, that is, 1 gram of gold required 0·01—0·02 gram of gelatin, whilst here, in a solution containing 0·08 gram of silver chromate per litre, 1 gram requires 0·02 gram of gelatin. In the case of the gold, the pro-

FIG. 1.



tection was exercised against 1 c.c. of 10 per cent. sodium chloride solution (1·7N). In the case of the silver chromate, a slight excess of either reactant or of both above the concentration limits given causes precipitation. Another electrolyte is, however, present, namely, potassium nitrate, the other product of double decomposition, but addition of 10 per cent. solution of this salt (1·0N) to any of the protected silver chromate failed to produce precipitation. From the shape of the graph in Fig. 2, dilution of any protected solution tends to increase the protection considerably, since the curve is very concave to the y-axis, and the graph of the concentrations in the diluted solution is a straight line joining the original point to the origin.

FIG. 2.



Experiments were now made on the production of periodic precipitation in 3 per cent. gelatin. From Fig. 2 it is seen that the concentration of silver chromate may be 0·0043N without precipitation. Actually, it was found that solutions made by diluting $N/50$-reactants to produce 0·005N-silver chromate precipitated on keeping, whilst those from $N/60$, producing 0·0042N, were stable. The initial solutions were made up by weighing, and the concentrations checked by titration. For some experiments to be described it was not desirable to have present any excess of either $Ag^{\cdot}$ or CrO_4''.

From the assumption that the "protected" silver chromate might be functioning as a colloid, it seemed reasonable to expect general precipitation to follow diffusion of either $Ag^{\cdot}$ or CrO_4'' into a gel containing the maximum amount of silver chromate. Conse-

quently, a series of tubes were half filled with 3 per cent. gelatin made $N/240$ with respect to silver chromate. The gel was allowed to set, and then solutions of silver nitrate and potassium chromate were poured above the gel. The results of a typical set of experiments are shown in tables IV and V below. It is to be noted that the earlier solutions are hypotonic to the salt solutions in the gel.

TABLE IV.

Solution above gel.	Result of diffusion beneath surface.
$N/250$-$AgNO_3$	Reddish haze 2—3 cm. below surface of gel.
$N/200$-$AgNO_3$	Intense reddish haze 1·5—2·5 below surface of gel.
$N/100$-$AgNO_3$	Traces of bands at 0·5, 1·0, 1·5.
$N/50$-$AgNO_3$	Bands at 0·2, 0·5, 0·9, 1·4, 2·1, 3·2, haze at 4·0.
$N/10$-$AgNO_3$	Fine bands 0—5·0.
$N/2$-$AgNO_3$	Thicker and closer bands 0—4·5, etc.

TABLE V.

$N/250$-K_2CrO_4	Haze 0·5—2·5.
$N/200$-K_2CrO_4	Haze 0·5—3·0.
$N/100$-K_2CrO_4	Thick band 0·5, trace at 0·9.
$N/50$-K_2CrO_4	Thick bands 0·2, 0·5, 0·8, 1·5.
$N/10$-K_2CrO_4	Thick bands 0·3, 0·6, 0·9, 1·5, 2·3.
$N/2$-K_2CrO_4	General precipitation with banded structure visible 0—4·9.

In all cases, there was a precipitate at the actual interface.

It will be seen that even under the conditions given, stratification took place. This means that in some manner or other the gel beneath a stratum of precipitate was cleared of the silver chromate. Whatever the cause, so to clear a perceptible space, diffusion must have occurred. In other words, the silver chromate did not function as a colloid with a slow rate of diffusion.

In some cases, the precipitate did not extend to the bottom of the test-tube, which was presumably due to exhaustion of the silver chromate by diffusion towards the precipitate. This was confirmed in the case of superimposed silver nitrate by the disappearance of the yellow colour from the gel. Where no stratification was recorded, hazes were sometimes noted, which were separated by clear intervals, and occasionally these hazes grew more intense in colour until a precipitate finally appeared. Where the more concentrated silver solutions were above the gels, there was frequently periodic precipitation above the surface, strata appearing for several mm. on the glass walls of the tube. In other cases, long, thin fibrils of silver chromate grew from the walls.

The next step was to find if the silver chromate diffused at all readily. Test-tubes were filled with the protected mixture as before, and the jelly was allowed to set. Above this, to a depth of 2·5 cm., was carefully poured and allowed to set some 3 per cent.

gelatin containing (*a*) $N/120$-potassium nitrate, (*b*) $N/240$-potassium nitrate, (*c*) no addition. In all cases, there appeared a cloudiness above the interface, which with the $N/120$-potassium nitrate advanced about 0·5 cm., but in the other cases appeared to extend as much as 1·5 cm. ultimately. After five days, $N/2$-silver nitrate and $N/2$-potassium chromate were poured on the top jelly. In all cases, there was precipitation at the top interface of silver chromate extending a millimetre or two downwards, and there appeared isolated portions of precipitate here and there before the second interface was reached. Precipitate did not form at the second interface, but some distance beneath, as much as 0·7 cm. in some cases. The precipitate obtained with the silver nitrate was in all cases much greater than that obtained with the potassium chromate, which is exactly the effect to be expected from the theory of the solubility product.

It seems noteworthy that the precipitate in the upper jelly should be concentrated at the surface. In one case, where a tube broke, the top of the jelly was cut off, and, on immersion in $N/2$-potassium chromate, the precipitate formed 2 mm. beneath the cut. This almost suggests previous adsorption at the air–jelly interface of the unprecipitated silver chromate, as well as subsequent diffusion towards the precipitate. It also suggests that in some way there might be a transfer to the top surface by detachment of part of the first jelly when the second was poured in. Although unlikely, this was tested. The second jelly was cooled before pouring in, so as to set almost immediately, and a layer was allowed to set before a second supply was poured in to make up the 2·5 cm. The effect was obtained as before. It was not obtained when the $N/2$-silver nitrate was poured on immediately, thus proving that diffusion to the new surface had not yet taken place. By reducing the depth of the top jelly, it was possible to obtain quite early precipitation in it by means of diffusing silver ion. Finally, jellies containing $N/240$-potassium nitrate were made to set in the bend of small U-tubes, and then $N/240$-silver chromate jelly set in one limb. After a week, $N/2$-silver nitrate was poured in the other limb, and a precipitate of silver chromate appeared at the surface of the jelly. There could be no chance of detachment of surface in this case.

These experiments lead to the conclusion that the silver chromate diffuses like a crystalloid. Two series of tubes were set up containing, respectively, $N/240$-silver chromate + $N/240$-potassium nitrate and $N/240$-potassium chromate + $N/240$-potassium nitrate, with superposed $N/240$-potassium nitrate jelly. At equal intervals, $N/2$-silver nitrate was poured on the top jelly in corresponding

tubes, and the precipitates obtained were very similar, suggesting that the diffusions were comparable in the two cases. The experiments on diffusion were performed both in the thermostat and at the ordinary temperature.

It is not yet certain whether the behaviour of the silver chromate is due to some property of the gelatin itself or to the impurities in it. In the 3 per cent. gelatin employed, the concentration of $Ca^{\cdot\cdot}$ would be $0{\cdot}012N$, which is considerable. On the other hand, in the very dilute solutions earlier examined, the concentration of $Ca^{\cdot\cdot}$ would be relatively negligible. Fig. 2 is evidently the solubility curve for silver chromate in gelatin solutions at 25°, and from it the solubility product may easily be calculated for different concentrations.

Our conclusions are that precipitation of silver chromate occurs according to the usual rules of the solubility product. By diffusion towards the precipitate, the next portion of the gel is cleared of the second ion more quickly initially than the precipitating ion can reach it in quantity, thereby setting up a concentration gradient, so that this ion must travel some distance before further precipitation takes place. It is obvious that the gel incidentally provides mechanical support for the precipitate.

The distance at which a second stratum appears is evidently dependent on the relative rates of diffusion of the precipitating ion, say, $Ag^{\cdot}$ and of the CrO''. The diffusion of the first ion may be hindered by the precipitate or by precipitation at the precipitate. The faster the second ion diffuses to the precipitate, the further from the precipitate will be the mean value of the concentration in the region of diffusion, and hence, under suitable conditions (that is, not too high concentration of one reactant, for example, potassium chromate, behind the precipitate), the further from the precipitate will be the place at which new precipitate forms. Diffusion is a very slow process, and in the case considered can only be accelerated by reducing the concentration to which diffusion proceeds, that is, the concentration at the precipitate. Bradford assumes this reduction is accomplished by adsorption, but although adsorption at the surface of the adsorbent is faster than diffusion, it cannot accelerate diffusion otherwise than is here indicated, and since simple continuous precipitation at the stratum would have the same effect, it is unnecessary at present to assume adsorption.

Summary.

(1) Observations have been made on the variation of the solubility of silver chromate with gelatin-concentration in aqueous solution at 25°.

(2) It is shown that the silver chromate does not behave as a protected colloid, but as a crystalloid, and that its precipitation follows the usual rules of the solubility product.

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XCV.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part II. The Dinitrotoluenes.*

By JAMES KENNER and MICHAEL PARKIN.

A REVIEW of the results obtained by previous workers on the reactivity of substituents in the benzene nucleus, as determined by the presence of nitro-groups in the ortho- or para-position led one of us (Kenner, T., 1914, **105**, 2717) to associate this influence with the meta-directive properties of this group, and it was suggested that ortho-para-directive groupings or atoms might confer mobility on substituents in the meta-position. Further, it was concluded that the displacement of such mobile substituents depended primarily on the formation of a molecular compound, which underwent rearrangement and decomposition, leading to the products actually isolated. In this way, the failure of the nitro-group to exert its usual steric effects was accounted for, but the action of such influences, for example, on the part of methyl groups, in inhibiting the formation of the necessary additive compound furnished a simple explanation of some exceptional cases which previously seemed inexplicable.

With the object of testing the validity of these conclusions, a qualitative study of the action of ammonia and sodium methoxide on 2:3-, 3:4-, and 2:5-dinitrotoluenes has been made.

Of the two nitro-groups in 2:3-dinitrotoluene, it is clear from the foregoing that the effect of the methyl group would be expected to make that in the 3-position the more mobile. A necessary preliminary of its displacement, however, is the formation of an additive compound with the 2-nitro-group, but this is sterically inhibited by the methyl and the 3-nitro-groups. As a result, the 3-nitro-group must take part in the preliminary reaction, and the 2-nitro-group be displaced. Experiment fully confirmed this inference, the respective products of the action of sodium methoxide

and of methyl-alcoholic ammonia being easily identified as pure 6-nitro-*o*-tolyl methyl ether and 3-nitro-*o*-toluidine.

The case of 3:4-dinitrotoluene is simpler, since the two nitro-groups are equally accessible for the purpose of the formation of the preliminary molecular compound. The influence of the methyl group again favours the displacement of the 3-nitro-group, and, indeed, the product of the action of methyl-alcoholic ammonia at 150° was found to consist to the extent of 93·5 per cent. of 4-nitro-*m*-toluidine, the remainder being in all likelihood 3-nitro-*p*-toluidine. The main product of the action of sodium methoxide was an insoluble compound, evidently of high molecular weight, and very probably a stilbene derivative of the type prepared by Green (T., 1908, **93**, 1721) from *p*-nitrotoluene. A small amount of 6-nitro-*m*-tolyl methyl ether was obtained; the oily portion of this product, which did not crystallise, may possibly have contained 2-nitro-*p*-tolyl methyl ether, since this compound is described as melting at 8·5° (de Vries, *Rec. trav. chim.*, 1909, **28**, 2), but the quantity available was too small for identification.

The results obtained with 2:5-dinitrotoluene show that in this case both the possible isomerides are produced. Whilst the 5-nitro-group may be expected to be the more mobile, it is not surprising that the steric influence of the methyl group above referred to asserts itself and sufficiently reduces the velocity of formation of the additive compound with the 2-nitro-group to permit of the 5-nitro-group taking an appreciable part in the preliminary reaction. When, therefore, 2:5-dinitrotoluene was heated with methyl-alcoholic ammonia at 160° for six hours, a period which sufficed for the completion of the reaction in the case of the 3:4-isomeride, about 45 per cent. of the dinitro-compound remained unchanged. By prolonging the reaction, a mixture of amines was produced, consisting of about 88 per cent. of 5-nitro-*o*-toluidine with 12 per cent. of 6-nitro-*m*-toluidine. On the other hand, the relatively small quantity of crystals which separated from the oily product of the action of sodium methoxide on the dinitrotoluene consisted of 4-nitro-*m*-tolyl methyl ether. Apparently, therefore, the influence of the methyl group is not sufficiently great completely to prevent the formation of the alternatively possible products.

The colour changes, indicative of the formation of an additive compound, which take place on adding ammonia to the three dinitrotoluenes are in accord with the explanations given above. 3:4-Dinitrotoluene at once gives a red coloration in the cold, the 2:5-compound gives a red colour only on warming, and the 2:3-compound gives only a yellow colour, even when the mixture is heated.

The experimental results are therefore easily explained in terms of the hypothesis previously advanced. This is also very largely true of the interesting data communicated by Holleman and his collaborators (*Rec. trav. chim.*, 1915, **35**, 1), and summarised below in regard to the dichloronitrobenzenes and the chlorodinitrobenzenes. In the table, the figures in clarendon type indicate the substituents which suffer displacement under the influence of sodium methoxide, diethylamine, or ammonia:

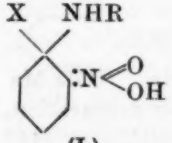
	Reaction constants at 85° (time in hours).			Reaction constants at 25° (time in hours).	
$NO_2:Cl:Cl$.	CH_3ONa.	$(C_2H_5)_2NH$.	$Cl:NO_2:NO_2$.	CH_3ONa.	NH_3.
1:2:4	19·41	0·027	**1:2:4**	90·6	0·0206
1:3:4	17·42	0·0044	**1:2:5**	33·5	0·00512
1:2:5	3·93	0·0067	**1:3:4**	26·22	0·00807
1:2:3	1·74	0·0016	**1:2:3**	6·0	0·0137
1:2:6	0·135	0·00024	**1:2:6**	2·76	0·0121

Considering first the results from the dichloronitrobenzenes, the displacement of the chlorine atom in the ortho-position with respect to the nitro-group in the 1:2:4-compound in preference to that in the para-position is particularly interesting. It is in accordance with the views now represented, but the fact that the reaction constant of *p*-chloronitrobenzene is greater than that of the ortho-compound led Holleman to expect that the para-atom would be displaced. It will be observed that the order of the constants observed with diethylamine differs slightly from those obtained with sodium methoxide, showing that the nature of the reagent cannot be neglected in considering the relative activities of such compounds. The order of the values obtained with sodium methoxide corresponds with that to be anticipated as a result of applying the considerations already discussed. Both the nitro-group and the second chlorine atom co-operate in rendering one of the chlorine atoms of the 1:2:4-isomeride mobile; in the 1:3:4-derivative, the influence of the 3-chlorine atom is contrary to that of the nitro-group, but there is no steric hindrance to the formation of the additive compound such as may very possibly occur in the case of the otherwise similar 1:2:5-derivative; in the 1:2:3-compound there is the added complication of steric hindrance by the chlorine atom in the 3-position to the later stages of the reaction, whilst the relative stability of the 1:2:6-isomeride is accounted for by the powerful steric hindrance to the formation of the initial compound.

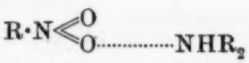
The chlorodinitrobenzenes are more interesting, since all three substituents are capable of displacement. Apparently, only one product is obtained in each case, and the result of displacement is

in every case in accord with anticipation, except that in the case of the 1:2:5-compound it is not possible to foresee which of the opposing influences discussed in connexion with 2:5-dinitrotoluene will be the stronger. The great divergence between the order of the values of the two sets of reaction constants suggests that in one or both series the nature of the nitro-derivative is not the chief determining factor in determining their relative activities, and little value can attach to their discussion from this point of view. Of the two series, the values obtained with sodium methoxide correspond the better with the views expressed above. A prominent feature of the quantitative results is the great increase in the magnitude of the constants over those of the corresponding dichloronitrobenzenes. Holleman illustrates this by a comparison of 2:4-dichloronitrobenzene with 4-chloro-*o*-dinitrobenzene (1:3:4), of 3:4-dichloronitrobenzene with 2-chloro-*p*-dinitrobenzene (1:2:5), and of 2:3-dichloronitrobenzene with 3-chloro-*o*-dinitrobenzene (1:2:3). Of each pair, the first suffers displacement of a chlorine atom, the second of a nitro-group in molecules otherwise identical, but the ratios of the respective constants at 25° are 800, 1000, and 2000. Similarly, the chlorodinitrobenzenes react with methyl-alcoholic ammonia at 100°, but the dinitrotoluenes were recovered practically unchanged after treatment under such conditions.

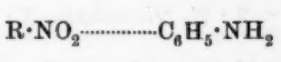
As regards the constitution of the intermediate compounds postulated in these reactions, arguments were advanced in the previous paper against the quinonoid formula (I), proposed by several workers, and preference was given to Werner's (II) or, alternatively, to Pfeiffer's formula (III):



(I.)



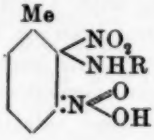
(II.)



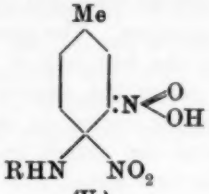
(III.)

The results since obtained would appear to strengthen the case against the quinonoid formula, which can offer no satisfactory explanation of the formation of one of the possible isomerides, either alone or in an overwhelmingly predominating amount. For example, in order to explain on this basis the formation of 3-nitro-*o*-toluidine from 2:3-dinitrotoluene, it appears necessary to assume that the methyl group exerts some directive influence, resulting in the formation of the compound (IV). In the case of 3:4-dinitrotoluene, however, such an influence would be expected to involve the formation of the product (V), from which 3-nitro-*p*-toluidine should be obtained.

Considerations of this kind appear to lead inevitably to the choice of some formula of the type (II) or (III).



(IV.)



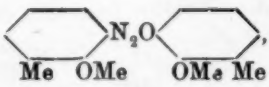
(V.)

EXPERIMENTAL.

The dinitrotoluenes were prepared according to the directions of Meisenheimer and Hesse (*Ber.*, 1919, **52**, 1161), whilst the strengths of sodium methoxide and ammonia solutions were those employed by Holleman (*loc. cit.*), in order that the results obtained in the two series of experiments might be comparable.

Action of Sodium Methoxide on 2:3-*Dinitrotoluene.*—2:3-Dinitrotoluene (1·5 grams) was heated for nine hours on the water-bath with a solution of sodium (0·2 gram) in methyl alcohol (5 c.c.). The product consisted of a dark oil, which distilled almost entirely at 140°/24 mm., leaving a small, tarry residue. There can be no doubt that the product was 6-nitro-*o*-tolyl methyl ether, since this compound, which is referred to by Hofmann and Miller (*Ber.*, 1881, **14**, 568) as a yellow liquid, was obtained as a golden-yellow oil (b. p. 134°/21 mm.) by the action of sodium methoxide on 2-chloro-3-nitrotoluene (Found: N = 8·53. Calc.: N = 8·38 per cent.).

2 : 2′-*Dimethoxy*-3 : 3′-*azoxytoluene*,



which was also produced in small amount in the above preparation, separated from alcohol in diamond-shaped prisms melting at 144° (Found: N = 9·86. $C_{16}H_{18}O_3N_2$ requires N = 9·79 per cent.).

Action of Ammonia on 2:3-*Dinitrotoluene.*—The dinitro-compound was quite unaffected by treatment on the water-bath with 2·5*N*-methyl-alcoholic ammonia (20 c.c.). The mixture was therefore heated under pressure for fifteen hours at 150—160°. The resulting solution, on evaporation, left a residue (m. p. 97°), which did not depress the melting point of 3-nitro-*o*-toluidine.

Reduction of 2 : 3-*Dinitrotoluene.*—2-Nitro-*m*-toluidine was obtained by Limpricht (*Ber.*, 1885, **18**, 1452) by reducing 2:3-dinitrotoluene with hydrogen sulphide in boiling alcoholic ammonia solution. As it was a possible product of the above reaction, it was decided to attempt its preparation.

(1) In an experiment by Mr. H. Burton, hydrogen sulphide was passed for three hours through a boiling solution of the dinitro-compound (3·6 grams) in alcohol (25 c.c.) to which ammonia solution (10 c.c.: D 0·880) had been added. The product obtained after filtration and evaporation was fractionally crystallised from alcohol. The main product, after recrystallisation from benzene, consisted of yellow prisms melting at 150°. Analysis showed it to be *dinitroditolyl sulphide*, $(C_6H_3Me{\cdot}NO_2)_2S$, most probably the 2:2′:6:6′-isomeride (Found: N = 8·92. $C_{14}H_{12}O_4N_2S$ requires N = 9·2 per cent.). The more readily soluble product, after recrystallisation from benzene, melted at 54°. Although Limpricht's base melted at 55°, it is uncertain whether our compound was 2-nitro-*m*-toluidine, since it was not acetylated under ordinary conditions. The quantity available was too small for analysis, and the course of the present work did not necessitate closer investigation.

(2) A solution of stannous chloride (11·4 grams) and hydrogen chloride (16 grams) in absolute alcohol (50 c.c.) was added drop by drop to a cold solution of 2:3-dinitrotoluene (3·64 grams) in alcohol (50 c.c.). After half an hour, the solution was diluted and extracted with ether. The residue, after evaporation of the ether, was resolved into its components by treatment with light petroleum. The more readily soluble consisted of unchanged dinitro-compound, whilst the sparingly soluble product (1·2 grams) separated from a mixture of ether and light petroleum in long, stout, deep red prisms melting at 106° (Found: N = 18·45. $C_{14}H_{12}O_4N_4$ requires N = 18·66 per cent.). The compound was therefore a *dinitroazotoluene*, probably the 2:2′:3:3′- rather than the 6:6′:2:2′-isomeride.

Action of Sodium Methoxide on 3:4-*Dinitrotoluene.*—The products obtained from 3:4-dinitrotoluene (3 grams) consisted of a black, insoluble product (0·8 gram), probably a stilbene derivative (see p. 853), a dark red, resinous product (0·5 gram) soluble in alkali, and an oil. From the latter, a few crystals separated after some weeks. These, after purification by draining on a porous tile and solution in light petroleum, were obtained as colourless plates melting at 53—57°. A mixture with an equal quantity of the original dinitrotoluene (m. p. 59—60°) softened at 40° and melted completely at 50°. The quantity available was too small for analysis, but there can be little doubt that the substance was 6-nitro-*m*-tolyl methyl ether, the description of which corresponds with our product, and of which the melting point is variously given as 51—52° (Reissert and Scherk, *Ber.*, 1898, **31**, 398), 60° (Fischer and Rigaud, *Ber.*, 1902, **35**, 1259), and 62° (Khotinsky

and Jacopson-Jacopmann, *Ber.*, 1909, **42**, 3099). 2-Nitro-*p*-tolyl methyl ether forms pale yellow crystals melting at 8·5° (de Vries, *loc. cit.*), and it is therefore possible that some of this was present in the portion of the oil which did not solidify.

Action of Ammonia on 3:4-*Dinitrotoluene.*—From the product obtained by heating 3:4-dinitrotoluene (1·82 grams) with 2·5*N*-methyl-alcoholic ammonia (32 c.c.) for six hours at 150° were obtained pure 4-nitro-*m*-toluidine (m. p. 109°; 1·1 grams), and a further quantity (0·15 gram) of impure product (m. p. 82°). By the application of Holleman's freezing-point method, it was shown that this corresponded with mixtures containing 4-nitro-*m*-toluidine with either 32 or 61 per cent. of 3-nitro-*p*-toluidine. Since the addition of the latter base to our product caused a rise in the temperature of solidification in agreement with the calculated, it contained 61 per cent. of this base.

4-*Nitro-o-tolyl Methyl Ether.*—The product of the interaction of 2-chloro-5-nitrotoluene and sodium methoxide, after isolation in the usual manner, crystallised from light petroleum in long, radiate needles melting at 63° (Found: N = 8·35. $C_8H_9O_3N$ requires N = 8·38 per cent.).

Action of Sodium Methoxide on 2:5-*Dinitrotoluene.*—By the action of sodium methoxide on 2:5-dinitrotoluene (3 grams), an oil (2 grams) was obtained, from which a quantity of crystals separated overnight; a further quantity separated when the oil was stirred with light petroleum. These, when collected and purified by crystallisation from light petroleum, melted at 55°, the melting point of 4-nitro-*m*-tolyl methyl ether (Reissert and Scherk, *loc. cit.*). A mixture with the original dinitro-derivative liquefied at the ordinary temperature, whilst that with 4-nitro-*o*-tolyl methyl ether melted at 28°. It is therefore clear that one of the products of the reaction was 4-nitro-*m*-tolyl methyl ether, but the other possible isomeride may also have been present, since the oil did not solidify completely even after some months.

6-*Nitro*-m-*toluidine.*—This compound was prepared according to the directions of Noelting and Stoecklin (*Ber.*, 1891, **24**, 564), who recommend steam-distillation of the products of nitrating *m*-toluidine until the distillate is no longer yellow. It was, however, found that 6-nitro-*m*-toluidine is slightly volatile in steam, and therefore the yellow colour does not completely disappear. When 16 litres of distillate, containing 11·7 grams of base, had been collected from the product of nitrating 32 grams of *m*-toluidine, the melting point of the crystals deposited, which had gradually risen during the distillation from 63° to 87°, suddenly rose to 133°, which was also the melting point of the residue in the distillation

flask. Although the authors named give 138° as the melting point, this could not be attained in the present case, either by repeated crystallisation or by purification of the base through its acetyl derivative, which was easily obtained by the addition of a drop of sulphuric acid to a mixture of the base with acetic anhydride. It separated from dilute alcohol in small prisms (m. p. 104°), and was easily hydrolysed by treatment with concentrated hydrochloric acid (Found: N = 14·20. Calc.: N = 14·4 per cent.).

2-*Nitro*-5-*nitrosotoluene*.—6-Nitro-*m*-toluidine (10 grams) was shaken for sixteen hours with Caro's acid (400 c.c.) from potassium persulphate (70 grams) and sulphuric acid (77 grams). The product (7 grams), after crystallisation from alcohol, melted at 113° (Found: C = 50·37; H = 3·59. $C_7H_6O_3N_2$ requires C = 50·60; H = 3·61 per cent.).

By oxidation with fuming nitric acid (10 parts), it was easily converted into 2:5-dinitrotoluene.

Action of Ammonia on 2:5-*Dinitrotoluene*.—The dinitro-compound (1 gram) was heated with alcoholic ammonia (32 c.c.) at 150° for fifteen hours. The residue obtained by evaporating the resulting solution was stirred with cold concentrated hydrochloric acid. The base precipitated from the acid solution by ammonia melted at 115—120°, but after crystallisation from dilute alcohol it melted at 127°, as did also its mixture with 5-nitro-*o*-toluidine. Since, on the other hand, its mixture with 6-nitro-*m*-toluidine melted at 114—115°, it is clear that the product in question was 5-nitro-*o*-toluidine. The low yield was due to the formation of a tarry product, which was insoluble in hydrochloric acid, and was not further investigated. According to measurements of the solidification points of mixtures of 5-nitro-*o*-toluidine with 6-nitro-*m*-toluidine, the crude base precipitated from acid solution contained about 88 per cent. of the former.

The authors wish to take this opportunity of expressing their grateful acknowledgments of the assistance afforded them by a grant from the Research Fund of the Chemical Society, and by Messrs. The British Dyestuffs Corporation (Blackley), Limited, in supplying them with *o*-toluidine.

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XCVI.—*Complex Metallic Ammines. Part III. Dichlorotetrapyridinecobalt Salts.*

By Thomas Slater Price.

In a previous communication (Price and Brazier, T., 1915, **107**, 1913), it has been shown that *trans*-dichlorodiethylenediaminecobalt salts give rise to peculiar additive compounds with certain organic dibasic acids. Evidence was obtained that this peculiarity is also shown by the *trans*-dibromodiethylenediaminecobalt salts. It is characteristic of these two series of salts that the chloride or bromide from which they are derived forms additive compounds with the respective halogen hydracids, namely,

$$1:6[Cl_2Co\,en_2]Cl,HCl,2H_2O$$

and $1:6[Br_2Co\,en_2]Br,HBr,2H_2O$. Dichlorotetrapyridinecobalt chloride and *trans*-dichlorotetramminecobalt chloride do not, however, form additive compounds with the halogen hydracids, their respective formulæ being $[Cl_2CoPy_4]Cl,6H_2O$ and

$$[Cl_2Co(NH_3)_4]Cl,H_2O,$$

and it was therefore of interest to see if the formation of additive compounds took place when their salts with dibasic organic acids were prepared. The dichlorotetrapyridinecobalt salts were chosen for examination, since they are fairly stable in aqueous solution (Werner and Feenstra, *Ber.*, 1906, **39**, 1538), whereas the dichlorotetramminecobalt salts rapidly change to chloroaquo- and diaquotetrammine compounds. Werner and Feenstra (*loc. cit.*) prepared dichlorotetrapyridinecobalt chloride by the action of chlorine on an aqueous solution containing cobalt chloride and pyridine. It being somewhat difficult, according to this method, to regulate the amount of chlorine entering into reaction, it was decided to generate the chlorine electrolytically in the presence of the solution of cobalt chloride containing pyridine, the necessary chlorine being provided by the addition of sodium chloride to the electrolyte. A divided cell was used, and the preparation was completely successful,* better yields of dichlorotetrapyridinecobalt chloride being obtained than by Werner and Feenstra's method.

The chloride thus prepared had the appearance described by Werner and Feenstra, and gave the correct analytical results, but

* When pyridine is replaced by ethylenediamine a mixture of dichlorodiethylenediaminecobalt chloride and triethylenediaminecobalt chloride appears to be formed. With diethylamine in place of pyridine an insoluble, amorphous green complex cobalt compound is produced, the composition of which seems to be variable and has not yet been elucidated.

when various tests were applied to its aqueous solution, some discrepancies were noticed. For example, Werner and Feenstra state that a 5 per cent. solution gives no precipitate with mercuric chloride, cobalt nitrate, or ferric chloride. With the specimen prepared electrolytically, however, a 5 per cent. solution could not be obtained at the ordinary temperature, but only an approximately 1 per cent. solution; this gave precipitates immediately with mercuric chloride, cobalt nitrate, and ferric chloride. In order to find an explanation of these discrepancies, a sample of the chloride was prepared according to Werner and Feenstra's method. It was found to give exactly the same reactions and have about the same solubility as the salt prepared electrolytically, so that the statements made by Werner and Feenstra are evidently in error.

In order to make certain that the chloride had been correctly characterised, other salts were prepared and analysed; these consisted of the nitrate (previously obtained by Werner and Feenstra), dithionate, benzylthiosulphate, and tetranitrodiamminecobaltate. In agreement with Werner and Feenstra, the thiocyanate and iodide could not be obtained.

One great difficulty experienced in the preparation of these salts has been to obtain them in the air-dry condition. When definitely crystalline, they separate in shining spangles, which felt together when collected, and the mass does not dry readily on a porous tile. The simpler salts are, as it happens, readily soluble in alcohol, and if the collected crystals, after being washed with water, are washed with a little alcohol and then with ether,* they no longer felt together. Even then, however, during the abnormally damp weather which has prevailed during the time this investigation has been in progress, it has been impossible to be quite certain that the salts were air-dry, so that estimations of the water of crystallisation were likely to give fictitious values. The nitrate was always found to contain more than the one molecule of water of crystallisation given by Werner and Feenstra; this difference may possibly be accounted for by the difference in the amount of moisture normally present in the air at Birmingham and Zürich, since Price and Brazier found similar discrepancies in the water of crystallisation of oxalatodiethylenediaminecobalt bromide and chloride (T., 1915, **107**, 1376, 1727).

In agreement with the fact that dichlorotetrapyridinecobalt chloride does not form an additive compound with hydrogen chloride, additive compounds with organic dibasic acids (oxalic, malonic, and thiodiacetic acids) were not obtained.

* Except where otherwise stated, this method of washing was always used.

Experimental.

Electrolytic Preparation of Dichlorotetrapyridinecobalt Chloride, $[Cl_2CoPy_4]Cl,6H_2O$.

The divided cell used consisted of a central anode compartment made from a glass cylinder with parchment paper tied over the lower end. This stood on a glass triangle in a beaker containing the catholyte and a platinum foil cathode. A rotating platinum electrode, similar to that described in Perkin's "Practical Methods of Electrochemistry," p. 198, was used as anode. The catholyte was a 5 per cent. solution of sodium chloride, to which sufficient hydrochloric acid was added from time to time during the electrolysis to keep it acid. The anolyte was prepared as follows: 20 grams of cobalt chloride hexahydrate and 5 grams of sodium chloride were dissolved in 60 c.c. of hot water; after cooling, the solution was placed in the anode compartment, and the anode started rotating. Thirty grams (31·5 c.c.) of pyridine were then added, and the current immediately switched on, the current density being 2 amperes per sq. dm. and current strength 1 ampere. Owing to the formation of complex ions, there was very little migration of cobalt ions to the catholyte, the simpler ions carrying most of the current. As electrolysis proceeded, the anolyte became darker and darker in colour, finally being very dark brown, and a sludge of green crystals formed. No cooling was necessary. The current was passed for the time theoretically necessary to give one atom of chlorine for each atom of cobalt taken (1 ampere for 3·4 hours), and then the contents of the anode compartment were poured into a beaker and allowed to remain overnight. The collected and washed crystals were dried on a porous tile. The yields obtained in three different experiments were 14·5, 13·8, and 14·8 grams respectively, the product being completely soluble in water.

When prepared according to Werner and Feenstra's method (*loc. cit.*), the same quantities of cobalt chloride and pyridine were taken, but only 30 c.c. of water. These authors state that a deep blue solution results when the pyridine is added to the cobalt chloride solution, but this is not the author's experience, a pink precipitate always forming. The yield of crude chloride obtained was 9·5 grams (Werner and Feenstra give 10 grams); the salt was contaminated with a small quantity of a pale green, insoluble compound, and was thus far from pure.

The purity of the electrolytic preparation may be gauged from the fact that, without recrystallisation, it gave Co = 10·06, whereas

$C_{20}H_{20}N_4Cl_3Co,6H_2O$ requires Co=10·00 per cent. One recrystallisation from water at 50—60°, containing a little hydrochloric acid, gave the analytically pure substance.

The nitrate, $[Cl_2CoPy_4]NO_3,xH_2O$, was readily obtained according to Werner and Feenstra's method, the crystals being plates rather than needles. It seemed impossible to obtain the salt in an air-dry condition; when dehydrated over phosphoric oxide in a vacuum desiccator,* one sample which, after recrystallisation, had been dried in the air for ten days, gave H_2O=14·02, whilst a second sample, after being dried for two days only, gave H_2O=13·15 per cent. For four molecules of water of crystallisation the loss should be 12·42, and for five molecules 15·06, per cent. The second sample gave Co=9·95, whereas $C_{20}H_{20}O_3N_5Cl_2Co,4H_2O$ requires Co=10·16 per cent. The dehydrated first sample gave Co=11·71, Cl=14·03, $C_{20}H_{20}O_3N_5Cl_2Co$ requiring Co=11·61, Cl=13·95 per cent.

Dichlorotetrapyridinecobalt dithionate, $[Cl_2CoPy_4]_2S_2O_6,xH_2O$, was precipitated almost quantitatively as a green, microcrystalline powder when a solution of 2 grams of sodium dithionate in 20 c.c. of water was added to a solution (at 50°) of 1 gram of the dichlorochloride in 50 c.c. of water containing a little hydrochloric acid. After drying in the air for three days, the salt lost 17·00 per cent. of water in a desiccator over phosphoric oxide, whereas after air-drying for thirty days it lost 14·57 per cent.

$$C_{40}H_{40}O_6N_8Cl_4S_2Co_2,xH_2O$$

requires H_2O=17·04 for x=12, and H_2O=14·62 per cent. for x=10. The dehydrated salt gave (Found: Co=11·08; Cl=13·27. $C_{40}H_{40}O_6N_8Cl_4S_2Co_2$ requires Co=11·21; Cl=13·48 per cent.).

The *double* salt of dichlorotetrapyridinecobalt chloride with mercuric chloride, $2[Cl_2CoPy_4]Cl,3HgCl_2$, was obtained as an insoluble, pale green, (?) microcrystalline precipitate when 50 c.c. of a 2 per cent. solution of the dichloro-chloride were mixed with 50 c.c. of a 2 per cent. solution of mercuric chloride, both solutions being at 50°. After cooling, the precipitate was collected, well washed with water, and dried in the air for three days (Found: Co=6·64; Hg=33·47. $C_{40}H_{40}N_8Cl_6Co_2,3HgCl_2$ requires Co=6·63; Hg=33·76 per cent.).

To prepare *dichlorotetrapyridinecobalt tetranitrodiamminecobaltate*, $[Cl_2CoPy_4][(NO_2)_4Co(NH_3)_2],xH_2O$, 1 gram of the dichloro-chloride dissolved in 70 c.c. of water was mixed with 1 gram of potassium tetranitrodiamminecobaltate dissolved in

* No loss of pyridine occurred. When such loss did take place it was immediately detected by the odour. These salts could not be dehydrated by heating, as pyridine was then driven off.

50 c.c. of water, both solutions being at 50°. The desired salt immediately separated (practically quantitatively) as a microcrystalline, pale yellowish-green precipitate. After being dried in the air for three days, it lost 3·19 per cent. of water in a desiccator over phosphoric oxide, whereas after air-drying for thirty days it lost 2·83 per cent. $C_{20}H_{26}O_8N_{10}Cl_2Co_2,xH_2O$ requires 2·43 per cent. for $x=1$ and 4·74 per cent. for $x=2$. (Anhydrous substance: Found: Co=16·40; Cl=9·68; N=19·16.

$C_{20}H_{26}O_8N_{10}Cl_2Co_2$

requires Co=16·31; Cl=9·80; N=19·37 per cent.)

Dichlorotetrapyridinecobalt benzylthiosulphate,

$[Cl_2CoPy_4]S_2O_3{\cdot}C_7H_7$,

is readily obtained in quantitative yield by mixing solutions of the dichloro-chloride (1·5 grams in 70 c.c. of water at 50°) and sodium benzylthiosulphate (1·5 grams in 30 c.c. of water). It is practically insoluble in water, and separates as a pale green, microcrystalline precipitate (Found: Co=9·14; N=8·45. $C_{27}H_{27}O_3N_4Cl_2S_2Co$ requires Co=9·08; N=8·63 per cent.).

The dichlorotetrapyridinecobalt salts of dibasic organic acids seem to be much more readily soluble in water than the chloride, with the result that the latter usually crystallises from solution when an attempt is made to prepare the organic salt. For example, 1·5 grams of the dichloro-chloride were readily soluble in 10 c.c. of water at 50° in the presence of 1·5 grams of thiodiacetic acid; on cooling, however, practically pure hydrated dichloro-chloride separated (Found: Co=9·96; Cl=17·84. Calc.: Co=10·00; Cl=18·04 per cent.). After dehydration over phosphoric oxide it gave Co=12·32, the theoretical percentage being 12·24. On the addition of solid sodium carbonate to the filtrate, a small quantity of a green precipitate was further obtained, which possibly consisted of the thiodiacetate, but when placed on a porous tile it lost pyridine and turned blue. Similarly, the hydrated dichloro-chloride separated when malonic acid was used, although in not quite as pure a condition as with thiodiacetic acid.

Attempts to prepare the oxalate did not give a pure product, although from different preparations salts giving the same analytical results were obtained. Thus, in one preparation, 1·5 grams of the dichloro-chloride and 2 grams of oxalic acid were dissolved in 60 c.c. of water at 50°, and the solution was cooled. Pale green crystals (microscopic plates) separated, which lost pyridine in a desiccator over phosphoric oxide, the residue turning blue (Found in air-dried sample: Co=9·65, 9·72; Cl=13·11 per cent.). In another preparation, the dichloro-chloride (1·5 grams) was dissolved in 40 c.c. of water at 50°, and then mixed with the oxalic acid

(2 grams) dissolved in 10 c.c. of water at 50°. The resulting salt gave Co = 9·62; Cl = 13·02 per cent. These analyses give the atomic proportion of cobalt to chlorine as 4 : 9, which is satisfied by the formula $3\{[Cl_2CoPy_4]C_2O_4H,4H_2O\},[Cl_2CoPy_4]Cl,6H_2O$, requiring Co = 9·78; Cl = 13·23 per cent. The salt could not be recrystallised without decomposition. Trituration with a saturated solution of oxalic acid did not lead to the isolation of a pure product. Other methods of preparation were not investigated, since there was no object in pursuing the matter further.

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XCVII.—*Arsinic Acids Derived from Guaiacol and Veratrole. Constitution of the Polyarsenides.*

By ROBERT GEORGE FARGHER.

THE literature of the organic compounds of arsenic contains no account of the arsinic acids derived from guaiacol and veratrole, though the conversion of *p*-hydroxyphenylarsinic acid into a dihydroxy-acid, presumably 3 : 4-dihydroxyphenylarsinic acid, by means of potassium persulphate has been claimed (D.R.-P. 271892). Trial of this reaction showed that the yield was poor and the product a mixture of 3 : 4-dihydroxyphenylarsinic acid with the unchanged acid. These were separable with difficulty, and their identity was most readily established by complete methylation and fractional crystallisation of the product.

3-Amino-4-hydroxyphenylarsinic acid and *3-amino-4-methoxyphenylarsinic acid* presented an alternative source, but the energetic treatment required to effect the decomposition of their diazo-compounds (compare D.R.-P. 95339; *J. Soc. Chem. Ind.*, 1898, **17**, 314; P., 1905, **21**, 206; French Pats., 167211, 228539) resulted in the almost entire destruction of the arsenical complex. The Bucherer reaction (compare *Ber.*, 1917, **50**, 101, where earlier references are given) also proved to be inapplicable.

The reaction devised by Bart (D.R.-P. 250264, 254092, 254345) therefore presented the most satisfactory method of obtaining the required substances. The preparation of the necessary amines was facilitated by the appearance of a communication by Cardwell and

Robinson (T., 1915, **107**, 257) dealing with 4- and 5-nitroguaiacol and 4-nitroveratrole.

These were reduced to the corresponding amines, which were diazotised and combined with sodium arsenite in alkaline solution, giving rise to 3-*hydroxy*-4-*methoxyphenylarsinic acid*, 4-*hydroxy*-3-*methoxyphenylarsinic acid*, and 3:4-*dimethoxyphenylarsinic acid* respectively.

All three acids were readily converted into the corresponding nitro-acids, and the reduction of these was investigated.

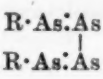
On complete reduction with sodium hyposulphite, only 5-*nitro*-4-*hydroxy*-3-*methoxyphenylarsinic acid* was found to undergo the normal reduction to the *arsenobenzene*. 5-*Nitro*-3-*hydroxy*-4-*methoxyphenylarsinic acid* yielded a product containing twice as much arsenic as required by the arsenobenzene formula, whilst 5-*nitro*-3:4-*dimethoxyphenylarsinic acid* did not give an insoluble reduction product, probably on account of the formation of a sulphamic acid (compare this vol., p. 372). It was therefore first reduced to the corresponding *amino*-acid. Further reduction also proceeded abnormally, sodium hyposulphite yielding a yellow, insoluble product containing arsenic in the proportion of three atoms to two benzene nuclei, and hypophosphorous acid a black, insoluble powder containing 93 per cent. of arsenic and probably consisting mainly of the free metalloid.

Bertheim has shown (*Chem. Zeit.*, 1914, **38**, 756; compare D.R.-P. 251104, 254226) that the reduction of molecular proportions of two arsinic acids leads solely to the unsymmetrical arsenobenzene.* More recently, Karrer (*Ber.*, 1916, **49**, 1648) has questioned the accepted mechanism of the reaction, and suggested that the symmetrical arsenobenzenes are first formed and then undergo "double decomposition." The latter suggestion amplifies rather than corrects the former, and indicates why, in spite of three possible, and indeed probable, primary reactions, the product consists solely of the unsymmetrical substance.

The generalisation was later extended (D.R.-P. 270354) to mixtures of an aromatic arsinic acid and an inorganic compound of arsenic, such as sodium arsenite, the products resembling those already referred to. The absence of full analytical data—included in the cases under discussion—has, however, left their composition in doubt, although Morgan ("Organic Compounds of Arsenic and

* At the author's request, Mr. W. H. Gray has confirmed Bertheim's statement by reducing molecular proportions of 1:3-benzodiazole-5-arsinic acid (T., 1919, **115**, 1372) and 3-amino-4-hydroxyphenylarsinic acid, the properties and composition of the product confirming the unsymmetric formulation.

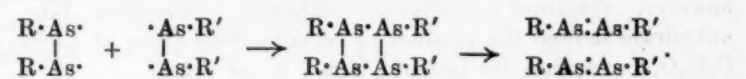
Antimony," p. 270) has suggested that they are possibly compounds of tervalent arsenic corresponding with the general types


and

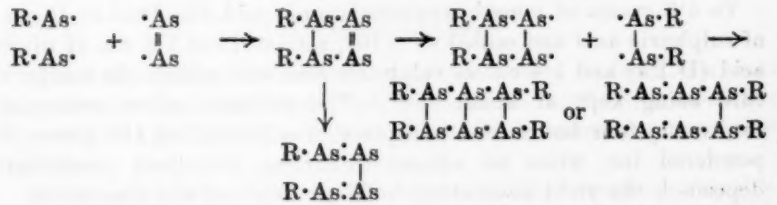
Of the polyarsenides described in the present communication, one—that obtained by the reduction of 5-nitro-4-hydroxy-3-methoxyphenylarsinic acid—supports the general formula R_2As_4, whilst another—that from 5-amino-3:4-dimethoxyphenylarsinic acid—agrees with a second type, R_2As_3 or R_4As_6. Of those prepared by Farbwerke vorm. Meister, Lucius & Brüning, one falls into each category.

The assumption of simultaneous reduction would require fission of the arsinic acid to precede reduction. The visual evidence suggests that, in the present instance, the reverse is the case, so the alternative mechanism has been assumed. It is supported by the observation that if a suspension of 3:3′-diamino-4:4′-dihydroxyarsenobenzene in the hyposulphite reduction mixture is treated with two molecular proportions of sodium arsenite and a further quantity of hyposulphite, the transition of the colour through reddish-brown finally to dull brown gradually takes place.

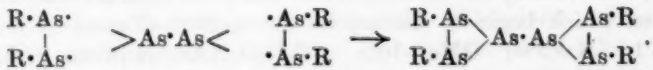
The reaction between two symmetrical arsenobenzenes to produce the unsymmetrical product may be represented as follows:



Its extension to the polyarsenical compounds permits of the formulation of the types R_2As_4 and R_4As_6 by the following stages:



or, alternatively,



The examination of the polyarsenides has, however, so far been too cursory to allow of any final statement as to their constitution,

and it should be emphasised that the homogeneity of the products, assumed on purely chemical grounds, would be difficult to determine satisfactorily in compounds relatively so unstable and insoluble.

Experimental.

p-*Methoxyphenylarsinic Acid.*

This was prepared by the methylation of *p*-hydroxyphenylarsinic acid (*Ber.*, 1914, **47**, 276). The melting point has been variously given by Michaelis (*Ber.*, 1887, **20**, 2051; *Annalen*, 1902, **320**, 299) as 159—160° and 203°, and by Bertheim as 179—180°. The acid crystallised from water in long, prismatic needles, which melted at 182° (corr.), and formed the anhydride at a temperature of 130°, the loss indicating the presence of a quarter of a molecule of water of crystallisation, only removed at the temperature of anhydride-formation (Found: loss at 130° = 9·6, 9·5. $C_7H_9O_4As,\frac{1}{4}H_2O$, for loss of $1\frac{1}{4}H_2O$, requires 9·5 per cent. In product: C = 39·4; H = 3·4. $C_7H_7O_3As$ requires C = 39·3; H = 3·3 per cent.).

As it was thought that this might account for the differences in melting point recorded above, the acid was boiled for an hour with acetic acid containing a little acetic anhydride, and then set aside, when fan-shaped clusters of needles separated. The melting point, however, remained unaltered, although conversion into the anhydride showed the product to be anhydrous (Loss at 130° = 8·1. $C_7H_9O_4As$ requires for loss of $1H_2O$ 7·8 per cent.).

3-*Nitro*-4-*methoxyphenylarsinic Acid.*

To 4·6 grams of *p*-methoxyphenylarsinic acid dissolved in 15 c.c. of sulphuric acid and cooled to −10°, a mixture of 1·4 c.c. of nitric acid (D 1·4) and 1·4 c.c. of sulphuric acid was added, the temperature being kept at about −8°. The mixture, after remaining for twenty-four hours in a cool place, was poured on 100 grams of powdered ice, when an almost colourless, flocculent precipitate deposited, the yield amounting to 95 per cent. of the theoretical.

3-*Nitro*-4-*methoxyphenylarsinic acid* is sparingly soluble in cold water, but readily so in hot, from which it separates in minute needles, which begin to decompose above 290° (Found: C = 30·0; H = 3·1; N = 5·0; OMe = 10·9. $C_7H_8O_6NAs$ requires C = 30·3; H = 2·9; N = 5·05; OMe = 11·2 per cent.). The acid was identical with that obtained by the methylation of 3-nitro-4-hydroxyphenylarsinic acid. The product from this reaction, however, contained much unchanged starting material. Separation was effected by

fractional crystallisation, the methylated acid being slightly the less soluble in water.

The *monosodium* salt crystallises in pale yellow needles containing $2H_2O$ (found: loss at 110° = 10·4. $C_7H_7O_6NAsNa,2H_2O$ requires $H_2O = 10·7$. In dried substance: Na = 8·0. $C_7H_7O_6NAsNa$ requires Na = 7·7 per cent.).

3-*Amino*-4-*methoxyphenylarsinic Acid*.

Five grams of 3-nitro-4-methoxyphenylarsinic acid were reduced in boiling methyl alcohol by 120 grams of 5 per cent. sodium amalgam. The solvent was removed by distillation, the residue dissolved in water, the solution decanted from mercury, and neutralised with hydrochloric acid. After concentration, the amino-acid gradually separated, and was purified by crystallisation from water, forming clusters of colourless needles, which melted and decomposed at 193° (corr.) (Found: N = 5·6; OMe = 12·7. $C_7H_{10}O_4NAs$ requires N = 5·7; OMe = 12·6 per cent.).

Many attempts were made to displace the amino-group by hydroxyl without success. When the diazotised solution was heated, no evolution of nitrogen took place, whilst experiments in which the temperature of the reaction was raised by the use of 10 per cent. sulphuric acid, a mixture of sodium sulphate and sulphuric acid, or a saturated solution of copper sulphate, led to almost complete decomposition. Similar results were obtained with 3-amino-4-hydroxyphenylarsinic acid. Experiments in which the acids were treated with sodium hydrogen sulphite were equally unsuccessful, and led to fission of the arsinic acid, the only isolable product being a small proportion of the unchanged acid.

4-*Aminoveratrole*.

The reduction of 4-nitroveratrole by tin and hydrochloric acid has already been described (*Bull. Soc. chim.*, 1896, [iii], **15**, 646; T., 1918, **113**, 28). The following method is, however, more satisfactory.

To a solution of 125 grams of crystalline sodium sulphide in a little water, 50 grams of 4-nitroveratrole (T., 1915, **107**, 257) were added, and the mixture was gently boiled for four hours, then cooled, and extracted with chloroform. The crude aminoveratrole was removed from the chloroform by dilute hydrochloric acid, and the combined extracts were basified, when most of the amine separated in a solid state and was collected, any base remaining in the filtrate being extracted by ether. The total yield amounted to 42 grams.

The acetyl derivative is very sparingly soluble in ether or light petroleum, more so in benzene, acetone, or ethyl acetate, and readily so in alcohol or hot water, from which it separates in glistening plates, which melt at 136° (corr.) (compare *Ber.*, 1896, **29**, 2690).

3:4-*Dimethoxyphenylarsinic Acid.*

A solution of 15 grams of aminoveratrole in 200 c.c. of 5 per cent. hydrochloric acid was diazotised with 7·1 grams of sodium nitrite, and added to 18 grams of arsenious oxide dissolved in 140 c.c. of 10 per cent. sodium hydroxide, nitrogen being immediately evolved. After several hours, the mixture was rendered strongly alkaline and warmed on the water-bath for half an hour, treated with charcoal, and acidified, when the acid gradually separated.

3:4-*Dimethoxyphenylarsinic acid* is very sparingly soluble in acetone, but readily so in alcohol or hot water, from which it separates in colourless, anhydrous, rhombic prisms. When placed in a bath at 170°, it melts at 192° (corr.), sintering from 187°. On slow heating, it sinters, but does not melt, between 180° and 190°. This behaviour is due to the readiness with which anhydride-formation takes place (Found: C = 36·4; H = 4·2; As = 28·6. $C_8H_{11}O_5As$ requires C = 36·6; H = 4·2; As = 28·6. Loss at 140° = 7·1. $C_8H_{11}O_5As$ requires for loss of $1H_2O$, 6·9 per cent.). The ammoniacal solution yields a voluminous precipitate of minute needles on boiling with calcium chloride, and an amorphous precipitate with magnesia mixture. With warm dilute hypophosphorous acid, a white, amorphous precipitate of 3:4:3′:4′-*tetramethoxyarsenobenzene* is obtained. When heated with hydrobromic acid at 100°, or with hydrochloric acid of varying concentrations at temperatures of 130° to 160° to effect partial demethylation, fission of the arsinic acid grouping takes place, only a small proportion of partly methylated acid being obtained.

5-*Nitro*-3:4-*dimethoxyphenylarsinic Acid.*

The preparation of this acid was carried out as described in the case of 3-nitro-4-methoxyphenylarsinic acid (p. 868), the yield amounting to 85 per cent. of the theoretical. It separates from boiling water in clusters of minute needles, which melt and decompose at 236° (corr.). Reduction with sodium hyposulphite leads to a reddish-brown solution, but no precipitate (Found: C = 31·1; H = 3·3; N = 4·6; As = 24·2. $C_8H_{10}O_7NAs$ requires C = 31·3; H = 3·3; N = 4·6; As = 24·4 per cent.).

The *monosodium* salt crystallises in glistening, flattened prisms, which lose their lustre when dried in the air and contain $6H_2O$ (Found: loss at 110° = 24·7. $C_8H_9O_7NAsNa,6H_2O$ requires $H_2O = 24·7$. In dried material, Na = 6·9. $C_8H_9O_7NAsNa$ requires Na = 7·0 per cent.).

The *barium hydrogen* salt crystallises as a matted mass of faintly yellow needles, which contain $3H_2O$ (Found: loss at 110° = 6·7. $(C_8H_9O_7NAs)_2Ba,3H_2O$ requires $H_2O = 6·7$. In dried material, Ba = 18·2. $(C_8H_9O_7NAs)_2Ba$ requires Ba = 18·3 per cent.).

Although the acid is more stable towards mineral acids than 3:4-dimethoxyphenylarsinic acid, its hydrolysis does not afford a suitable means of preparing the corresponding partly methylated and demethylated acids. At 160° with concentrated hydrochloric acid, it is largely decomposed, but at 130° slow hydrolysis of the methoxyl groups takes place, and crystallisation of the product yields from the more soluble fractions a proportion of a partly methylated acid, separating from water in slender prisms and melting and decomposing at about 254° (corr.). It is apparently identical with *5-nitro-3-hydroxy-4-methoxyphenylarsinic acid* (p. 874) (Found: C = 28·9; H = 3·0; OMe = 11·0. $C_7H_8O_7NAs$ requires C = 28·7; H = 2·75; OMe = 10·6 per cent.).

5-Amino-3:4-dimethoxyphenylarsinic Acid.

The foregoing acid was reduced by ferrous hydroxide in alkaline solution (compare *J. Amer. Chem. Soc.*, 1918, **40**, 1581), the yield amounting to about 85 per cent. of the theoretical. *5-Amino-3:4-dimethoxyphenylarsinic acid* dissolves sparingly in cold water or alcohol, but readily in dilute mineral acids or hot water, from which it separates in radiating clusters of needles melting and decomposing at 173° (corr.). The solution in dilute hydrochloric acid gives a bright red coloration with a trace of potassium dichromate, and, after treatment with nitrous acid, a deep red coloration with sodium-β-naphthoxide. The aqueous solution develops a reddish-brown colour with ferric chloride. The ammoniacal solution gives no precipitate on warming with magnesia mixture or with barium chloride, but with calcium chloride a heavy, crystalline precipitate (Found: N = 5·0; As = 27·3. $C_8H_{12}O_5NAs$ requires N = 5·05; As = 27·05 per cent.).

Reduction of 5-Amino-3:4-dimethoxyphenylarsinic Acid.

(*a*) *With Sodium Hyposulphite.*—The reduction was carried out as described in the case of 5-nitro-4-hydroxy-3-methoxyphenylarsinic acid (p. 873). The pale yellow precipitate deepened in colour as

the reaction proceeded. It was collected, washed very thoroughly with water and with alcohol, and dried in a vacuum, first at the ordinary temperature, and finally at 60° for analysis. The ratio of arsenic to the other elements present indicated 3 atoms of arsenic to 2 benzene nuclei. It dissolves sparingly in the usual organic solvents, but readily in dilute acids (Found: C=37·3, 37·3; H=4·0, 3·9; N=5·2; As=41·4. $C_{16}H_{20}O_4N_2As_3$ requires C=36·3; H=3·8; N=5·3; As=42·5 per cent.).

(*b*) *With Hypophosphorous Acid.*—Reduction with dilute hypophosphorous acid at 60° yielded a black precipitate, which was isolated as in the previous instance (Found: As=93·0; C=2·6, 2·9; H=0·54, 0·60).

The composition of these products is discussed in the introduction.

4-Hydroxy-3-methoxyphenylarsinic Acid.

A suspension of 25·2 grams of 4-nitroguaiacol in 90 c.c. of concentrated hydrochloric acid was reduced by the gradual addition of 42 grams of tin. The resulting solution was freed from tin, diazotised with 12 grams of sodium nitrite, and added to an ice-cold solution of 27 grams of arsenious acid in 210 c.c. of 10 per cent. sodium hydroxide, the solution being maintained distinctly alkaline. As soon as the evolution of nitrogen ceased, the product was heated for half an hour on the water-bath, acidified to methyl-orange by means of hydrochloric acid, treated with charcoal to remove coloured impurities, evaporated to dryness under diminished pressure, and extracted with alcohol. The extract, amounting to about 25 grams, was dissolved in boiling water, when, after separation of a small quantity of a very sparingly soluble substance (*A*), 12·5 grams of *4-hydroxy-3-methoxyphenylarsinic acid* were obtained. The acid is sparingly soluble in cold water or alcohol, but readily so in acetic acid or in hot water, from which it separates in stout, glistening, rhombic prisms containing $1H_2O$. After drying at 110°, it melts at 190° (corr.) (Found: loss at 110°=7·1. $C_7H_9O_5As,H_2O$ requires 6·8. In dried material, C=34·2; H=3·8; As=30·3. $C_7H_9O_5As$ requires C=33·9; H=3·7; As=30·2 per cent.). The ammoniacal solution gives no precipitate on boiling with barium chloride or magnesia mixture, but yields a crystalline precipitate of the *calcium* salt with calcium chloride. On warming the acid with a dilute solution of hypophosphorous acid, a colourless precipitate of *4:4′-dihydroxy-3:3′-dimethoxyarsenobenzene* is obtained.

The *acetyl* derivative crystallises from ethyl acetate containing a little alcohol in colourless, glistening plates, which melt at 186° (corr.), sintering from 182°. It is readily soluble in water or

alcohol, but sparingly so in ether or ethyl acetate (Found: C=37·5; H=4·1. $C_9H_{11}O_6As$ requires C=37·25; H=3·8 per cent.).

The sparingly soluble material (*A*), which was isolated only in minute quantity, proved to be 4:4′-*dihydroxy*-3:3′-*dimethoxydiphenylarsinic acid*. It separated from much water in radiating clusters of minute prisms containing $1\frac{1}{2}H_2O$, and melted at 234° (corr.), sintering from 227°. The ammoniacal solution of the acid gave a precipitate on warming with barium chloride, but not with magnesia mixture (Found: loss at 110°=6·7. $C_{14}H_{15}O_6As,1\frac{1}{2}H_2O$ requires 7·0. In dried material, C=47·3; H=4·4; As=21·2. $C_{14}H_{15}O_6As$ requires C=47·5; H=4·3; As=21·2 per cent.).

5-Nitro-4-hydroxy-3-methoxyphenylarsinic Acid.

The nitration of 4-hydroxy-3-methoxyphenylarsinic acid was carried out as already described (compare p. 868). Separation did not take place until the bulk of the mineral acid was neutralised by the addition of anhydrous sodium carbonate, when 3·2 grams of the nitro-acid were obtained. On crystallisation from boiling water, it formed glistening leaflets, which decomposed gradually above 260° without melting (Found: As = 25·5; N = 4·8. $C_7H_8O_7NAs$ requires As=25·6; N=4·8 per cent.).

On warming with a dilute solution of hypophosphorous acid, a bright yellow, granular precipitate of 5:5′-*dinitro*-4:4′-*dihydroxy*-3:3′-*dimethoxyarsenobenzene* was obtained.

5:5′-Diamino-4:4′-dihydroxy-3:3′-dimethoxyarsenobenzene.

To a solution of 3·5 grams of the above acid in 60 c.c. of water and 12 c.c. of 2*N*-sodium hydroxide was added a solution of 30 grams of sodium hyposulphite and 10 grams of magnesium chloride in 170 c.c. of water. The mixture was heated in an atmosphere of carbon dioxide at 60° for one and a-half hours, the arsenobenzene then collected, washed with water, dissolved in methyl alcohol containing hydrogen chloride, and the hydrochloride precipitated by the addition of dry ether. The product amounted to 2·1 grams of a faintly yellow powder, readily soluble in water and methyl alcohol, less so in ethyl alcohol, and insoluble in ether or acetone. The aqueous solution reacts faintly acid to methyl-orange. When dried to constant weight in a vacuum over sulphuric acid, it retains solvent equivalent to two molecules of water. It decomposes sharply at 186° (corr.). The addition of dilute sulphuric acid to the aqueous solution does not cause precipitation of the sulphate, but concentrated hydrochloric acid causes precipitation of the *hydrochloride* (Found: As=27·9; N=5·1;

Cl = 12·7. $C_{14}H_{16}O_4N_2As_2,2HCl,2H_2O$ requires As = 28·0; N = 5·2; Cl = 13·2 per cent.). This substance was submitted to biological test by Dr. R. A. O'Brien, of the Wellcome Physiological Research Laboratories, the results indicating that it was only slightly more toxic than salvarsan.

3-Hydroxy-4-methoxyphenylarsinic Acid.

This acid was prepared from 5-nitroguaiacol in the same manner as 4-hydroxy-3-methoxyphenylarsinic acid (p. 872) was obtained from 4-nitroguaiacol. From 21 grams of the nitroguaiacol, 8 grams of the pure acid were obtained. *3-Hydroxy-4-methoxyphenylarsinic acid* separates from water in short, stout, flattened prisms containing one molecule of the solvent, which is lost at 110°. It then melts at 189° (corr.). The pure acid dissolves sparingly in alcohol or the other usual organic solvents (Found: loss at 110° = 7·3. $C_7H_9O_5As,H_2O$ requires 6·8. In dried material, C = 34·2; H = 3·8; As = 30·1. $C_7H_9O_5As$ requires C = 33·9; H = 3·7; As = 30·2 per cent.). The ammoniacal solution gives no precipitate on boiling with barium chloride or magnesia mixture, but yields a precipitate with calcium chloride. On warming with a dilute solution of hypophosphorous acid, the acid yields a colourless precipitate of *3 : 3′-dihydroxy-4 : 4′-dimethoxyarsenobenzene.*

The *acetyl* derivative crystallises from benzene containing a little alcohol in woolly needles, which decompose gradually above 200°. It is readily soluble in water, alcohol, or ethyl acetate, but very sparingly so in benzene or light petroleum (Found: C = 37·5; H = 4·0. $C_9H_{11}O_6As$ requires C = 37·25; H = 3·8 per cent.)

5-Nitro-3-hydroxy-4-methoxyphenylarsinic Acid.

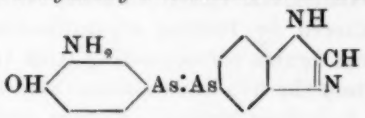
The preparation of this acid was carried out in a similar manner to that of 5-nitro-4-hydroxy-3-methoxyphenylarsinic acid (p. 873); the yield amounted to 80 per cent. of the theoretical. The acid crystallises from water, in which it is somewhat sparingly soluble, in stellate clusters of prismatic needles, which melt at 252° (corr.), darkening gradually above 220° (Found: As = 25·6; N = 5·0. $C_7H_8O_7NAs$ requires As = 25·6; N = 4·8 per cent.). On reduction with warm hypophosphorous acid, it yields a bright yellow precipitate of *5 : 5′-dinitro-3 : 3′-dihydroxy-4 : 4′-dimethoxyarsenobenzene.*

Reduction of 5-Nitro-3-hydroxy-4-methoxyphenylarsinic Acid.

The reduction was carried out, using sodium hyposulphite, as already described. The pale yellow precipitate first formed

gradually darkened to brick-red as the reaction proceeded. It was collected, washed thoroughly with water, and dissolved in methyl alcohol containing hydrogen chloride, forming a blood-red solution, which deposited a reddish-brown precipitate of the *hydrochloride* on addition of ether. Analysis indicated that the product contained 2 atoms of arsenic to each benzene nucleus (Found: C = 25·9; H = 3·3; N = 4·1; Cl = 10·5; As = 45·6. $C_{14}H_{16}O_4N_2As_4,2HCl$ requires C = 25·9; H = 2·8; N = 4·3; Cl = 10·9; As = 46·2 per cent.).

3′-Amino-4′-hydroxy-1 : 3-diazole-5 : 1′-arsenobenzene,



A mixture of molecular proportions of 3-amino-4-hydroxyphenylarsinic acid and 1 : 3-benzodiazole-5-arsinic acid was reduced with sodium hyposulphite in the manner previously described. The product was converted into the hydrochloride by solution in methyl alcohol containing hydrogen chloride, and precipitation by ether. The yield amounted to about 85 per cent. of the theoretical.

The *hydrochloride* forms a pale yellow powder, readily soluble in water or methyl alcohol, less so in ethyl alcohol, and almost insoluble in ether or acetone. After drying for several hours in a vacuum over sulphuric acid, it retains solvent approximating to 3 molecules of water of crystallisation, of which one is lost at 60° and a second at 100° in a vacuum. On heating, it decomposes at 206° (corr.) (Found: C = 32·1; H = 3·8; N = 8·3; As = 30·4; Cl = 14·0. $C_{13}H_{11}ON_3As_2,2HCl,3H_2O$ requires C = 31·1; H = 3·8; N = 8·4; As = 29·9; Cl = 14·1 per cent. Loss at 60° in a vacuum = 3·7. Loss of $1H_2O$ requires 3·6. Loss at 100° in a vacuum = 7·3. Loss of $2H_2O$ requires 7·2 per cent.).

The *base* dissolves readily and completely in sodium hydroxide or in methyl alcohol containing hydrogen chloride, thus differing distinctly from 5 : 5′-arseno-1 : 3 : 1′ : 3′-benzodiazole (T., 1919, **115**, 1372), which dissolves but sparingly in the former and is quite insoluble in the latter.

In conclusion, the author would thank Mr. F. P. Walton for assistance in the analysis of a number of the compounds described in the investigation.

WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C. 1. [*Received, May 19th*, 1920.]

XCVIII.—2 : 3 : 6-*Trinitrotoluene: a New Synthesis.*

By Oscar Lisle Brady and Arthur Taylor.

2 : 3 : 6-Trinitrotoluene was the last of the six isomeric trinitrotoluenes to be obtained. Molinari and Giua (*Zeitsch. ges Schiess. u. Sprengstoffw.*, 1914, **9**, 239), from the oily residues obtained in the purification of commercial trinitrotoluene, isolated a compound (m. p. 79·5°), unaltered by further crystallisation from alcohol, which gave analytical figures corresponding with trinitrotoluene.

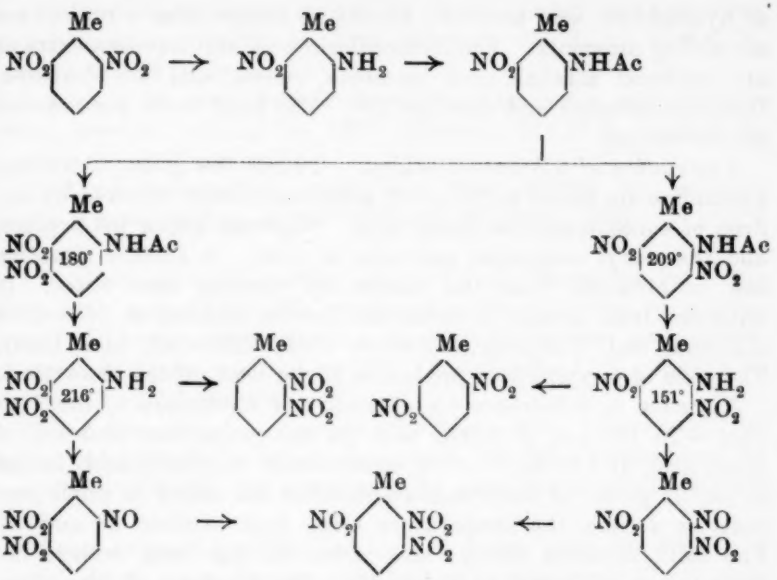
As this differed from the five known isomerides, it was considered by them to be the 2 : 3 : 6-compound. Körner and Contardi, however (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339), synthesised this compound from 2 : 4 : 6-trinitrotoluene by the following series of transformations: 2 : 4 : 6-trinitrotoluene ⟶ 2 : 6-dinitro-*p*-toluidine ⟶ 3-bromo-2 : 6-dinitro-*p*-toluidine ⟶ 3-bromo-2 : 6-dinitrotoluene ⟶ 2 : 6-dinitro-*m*-toluidine ⟶ 2 : 3 : 6-trinitrotoluene.

The 2 : 3 : 6-trinitrotoluene obtained in this way melted at 111°. Molinari and Giua's compound probably consisted of a mixture of 2 : 3 : 4- and 3 : 4 : 6-trinitrotoluenes, as in the separation of the mixture of these compounds, obtained by the nitration of *m*-nitrotoluene, by crystallisation from alcohol, a substance is obtained of approximately the melting point given by Molinari and Giua which crystallises from alcohol unchanged, but can be further fractionated into its two components by alternate crystallisation from acetic acid and from alcohol. This substance, of constant melting point, seems to be a loose, molecular compound of the two isomerides, as there is evidence of the existence of a compound of this melting point from the binary fusion diagram of 2 : 3 : 4- and 3 : 4 : 6-trinitrotoluenes (private communication from Dr. W. H. Gibson).

Körner and Contardi state that they have found conditions of reduction under which 2 : 4 : 6-trinitrotoluene gives a 60 per cent. yield of 2 : 6-dinitro-*p*-toluidine and promise a description in a subsequent paper. This has not yet been published and, as the usual means of reduction give poor yields, an alternative method has been devised for the preparation of 2 : 3 : 6-trinitrotoluene from 2 : 6-dinitrotoluene.

The reactions involved are summarised on p. 877.

The yields are satisfactory at all stages of the process, and a considerable quantity of 2 : 3 : 6-trinitrotoluene has been prepared by this method.



The mixture of the two dinitrotoluidines obtained by the nitration of 6-nitroaceto-*o*-toluidide and subsequent hydrolysis has been separated, and the dinitrotoluidines have been oriented by elimination of the amino-group and conversion into 2 : 3- and 2 : 5-dinitrotoluenes. This separation is not necessary for the synthesis of the 2 : 3 : 6-trinitrotoluene, as both compounds are converted into it in the subsequent operations.

EXPERIMENTAL.

Reduction of 2 : 6-*Dinitrotoluene.*—Although the preparation of 6-nitro-*o*-toluidine by the reduction of 2 : 6-dinitrotoluene has been mentioned by Cunerth (*Annalen*, 1874, **172**, 223), Bernthsen (*Ber.*, 1882, **15**, 3017), Noelting (*Ber.*, 1904, **37**, 1018), and Tatschaloff (*J. pr. Chem.*, 1902, [ii], **65**, 239), no experimental details are given. The following method has been found to give good yields. To 50 grams of 2 : 6-dinitrotoluene in 100 c.c. of boiling alcohol are added gradually 280 c.c. of ammonium sulphide (15 per cent.), the mixture being shaken thoroughly between each addition. When all the ammonium sulphide has been added, the mixture is heated on the water-bath for fifteen minutes and then cooled. The precipitate is collected, washed with water, extracted with hot dilute hydrochloric acid, and the solution filtered. The residue, consisting of the sparingly soluble hydrochloride of the base and sulphur, is repeatedly extracted with hot water containing a small quantity

of hydrochloric acid until the filtrate no longer gives a precipitate on adding ammonia. The hydrochloric acid and aqueous extracts are rendered alkaline with ammonia, cooled, and the 6-nitro-*o*-toluidine collected and dried at 70°. The yield is 80 per cent. of the theoretical.

Acetylation of 6-Nitro-o-toluidine.—Twenty-five grams of 6-nitro-*o*-toluidine are added to 35 c.c. of acetic anhydride, followed by one drop of concentrated sulphuric acid. Vigorous action takes place, and the acetyl compound separates at once. A further quantity can be obtained from the filtrate by pouring into water. It separates from alcohol in colourless needles melting at 163—164° (Lellman and Würthner, *Annalen*, 1885, **228**, 241, give 158°). The yield of recrystallised product is 80 per cent. of the theoretical.

Nitration of 6-Nitroaceto-o-toluidide and Hydrolysis of the Product.—To 175 c.c. of mixed acid (in the proportion of 5 c.c. of nitric acid, D 1·5, to 8 c.c. of concentrated sulphuric acid) cooled in ice, 25 grams of 6-nitroaceto-*o*-toluidide are added in small portions at a time, the temperature being kept between 4° and 7°. The solid dissolves slowly, and when all has been added, the temperature is allowed to rise to 12°. By this time, all the nitroacetotoluidide will have dissolved, and the product is slowly poured into a litre of water with thorough stirring. A pure, white product is precipitated in theoretical yield. This is collected, washed, dried, and 31 grams are dissolved in 100 c.c. of concentrated sulphuric acid and warmed on the water-bath for two hours. The mixture is cooled and poured into cold water, when a mixture of 5 : 6- and 3 : 6-dinitro-*o*-toluidines is precipitated in theoretical yield as a bright orange-yellow, crystalline material melting at 138—200°.

Separation of the Dinitro-o-toluidines.—By fractional crystallisation of the mixed dinitrotoluidines, a compound (m. p. 216°) is obtained, which was proved to be 5 : 6-dinitro-*o*-toluidine (see below). It is not possible to obtain the other isomeride pure by this method, and repeated crystallisation of the mixed acetyl derivatives gives a compound melting at 180°, which, however, on hydrolysis yields 5 : 6-dinitro-*o*-toluidine.

The more readily soluble amino-compound may be obtained, however, by dissolving the mixture of amines in hot glacial acetic acid and cooling slowly. Two kinds of crystals separate, namely, fine yellow needles and large orange prisms and, after filtering and washing with light petroleum, these can be readily separated by sieving. The orange crystals, when recrystallised from alcohol, yielded 3 : 6-dinitro-*o*-toluidine (m. p. 151°), previously obtained by Körner and Contardi (*loc. cit.*) by the action of ammonia on 2 : 3 : 6-trinitrotoluene, but not fully described.

5 : 6-*Dinitro-o-toluidine* crystallises from alcohol in fine, deep yellow needles melting at 216° (Found: N = 21·3. $C_7H_7O_4N_3$ requires N = 21·3 per cent.).

5 : 6-*Dinitroaceto-o-toluidide* crystallises from acetic acid in large white crystals melting at 180° (Found: N = 17·4. $C_9H_9O_5N_3$ requires N = 17·6 per cent.).

3 : 6-Dinitro-*o*-toluidine crystallises from alcohol in brilliant orange prisms melting at 151° (Found: N = 21·5. Calc.: N = 21·3 per cent.).

3 : 6-*Dinitroaceto-o-toluidide*, obtained from the above by treatment with acetic anhydride in the presence of a trace of concentrated sulphuric acid, crystallises from alcohol in very pale yellow, microscopic prisms melting at 209° (Found: N = 17·5. $C_9H_9O_5N_3$ requires N = 17·6 per cent.).

Orientation of the Dinitro-o-toluidines.—The position of the second nitro-group in these compounds has been determined by conversion into the dinitrotoluenes by elimination of the amino-group.

Of the compound melting at 216°, 2 grams were dissolved in a mixture of 10 c.c. of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) and 40 c.c. of absolute alcohol (freshly distilled over calcium oxide), and the mixture was heated on the steam-bath. Six grams of finely powdered, dried sodium nitrite were added in small portions with vigorous shaking. Most of the alcohol was then distilled off, water added, and the mixture distilled in a current of steam. The dinitrotoluene which distilled was collected, and, after recrystallisation from dilute alcohol, proved to be 2 : 3-dinitrotoluene from its melting point and mixed melting point with another sample. The compound melting at 216° is therefore 5 : 6-dinitro-*o*-toluidine.

In a similar way, 2 : 5-dinitrotoluene was obtained from the compound melting at 151°, which is accordingly 3 : 6-dinitro-o-toluidine.

Preparation of 2 : 3 : 6-*Trinitrotoluene.*—For the preparation of the trinitrotoluene, it is not necessary to separate the dinitro-*o*-toluidines, as both these compounds, on displacement of the amino- by the nitro-group, yield the same derivative.

Two methods of conversion were investigated, namely, introduction of the nitro-group through the diazonium nitrate (compare Witt, *Ber.*, 1909, **42**, 2953) and direct oxidation of the amino-group with Caro's acid, followed by nitric acid.

Of these, the first, under varying conditions, was completely unsuccessful, but no difficulty was experienced with the second.

To a solution of Caro's acid, prepared from 60 grams of finely powdered ammonium persulphate and 44 c.c. of concentrated

sulphuric acid, the mixture being finally poured on 120 grams of crushed ice, is added a solution of 12 grams of the dinitrotoluidines in 36 c.c. of concentrated sulphuric acid. A yellow solid separates at once, and the mixture is allowed to remain, with frequent shaking, for some days. At the end of that time the mixture of dinitronitrosotoluenes is collected and dropped in small quantities at a time into 100 c.c. of nitric acid (D 1·5) heated on the water-bath. When nitrous gases are no longer evolved and the liquid assumes a pale colour, it is diluted somewhat and cooled, when the 2:3:6-trinitrotoluene separates in colourless needles. The compound, after being collected and washed with water, is almost pure, but may be recrystallised from alcohol.

The yield of 2:3:6-trinitrotoluene prepared in this way is from 50 to 60 per cent. of the 2:6-dinitrotoluene employed.

In conclusion, the authors wish to express their thanks to the Director of Artillery for permission to publish these results.

RESEARCH DEPARTMENT,
ROYAL ARSENAL, WOOLWICH. [*Received, June 22nd,* 1920.]

XCIX.—*The Effect of Reducing Agents on Tetranitromethane, and a Rapid Method of Estimation.*

By AILEEN BAILLIE, ALEXANDER KILLEN MACBETH, and NORAH IRENE MAXWELL.

PREVIOUS work by one of us (T., 1915, **107**, 87) indicated that tetranitromethane contained one labile nitro-group, and it appeared likely that this would be removed in reduction, so that guanidine seemed the most probable product of extreme reduction. Acid reduction experiments with tin and nickel-coated zinc carried out by Rakshit (*J. Amer. Chem. Soc.*, 1914, **36**, 1221) resulted in the production of guanidine. A study of alkaline and electrochemical reduction methods has been undertaken by us, and in this paper the effect of some alkaline reducing agents is recorded. It is hoped to communicate later the results of electrochemical methods.

The reductions now described have resulted in the removal of the labile "nitroite" group, with the production of salts of nitroform, which may be conveniently and safely prepared by the methods described. The procedure consisted in agitating the nitro-

compound with aqueous solutions of the reducing agents containing a requisite amount of potassium hydroxide, which neutralises the nitroform produced, precipitating it as the sparingly soluble potassium salt. The solutions are thereby prevented from becoming acid, and secondary action with the reducing agent is avoided. Aqueous potassium hydroxide itself attacks tetranitromethane, with the formation of the potassium salt of nitroform, together with nitrate, nitrite, and carbonate of potassium, the quantities of which vary with concentration. The decomposition in such case, however, is much slower than when a reducing agent is present, and in the latter case the tetranitromethane is generally all converted into nitroform without the loss entailed in the formation of potassium carbonate.

Results have been obtained, amongst others, with sodium sulphite, potassium sulphite, sodium potassium tartrate, and hydrazine. In all cases, the nitroform salt has been identified by estimation of the percentage of potassium contained in the salt recrystallised from water; this was decomposed by sulphuric acid and the potassium weighed as sulphate.

Other reducing agents have also been tried with success; potassium phosphite and potassium sulphide may be mentioned as instances. In the case of the sulphide, much sulphur is precipitated, from which the nitroform salt is removable only with some difficulty. Aqueous solutions of sulphur dioxide do not attack tetranitromethane even after long-continued shaking. Ammonium sulphide readily decomposes it, but in this case the reduction seems to be carried past the nitroform stage, and the products, as yet, have not been identified.

Sodium Sulphite.—On shaking an aqueous solution of sodium sulphite with tetranitromethane, the solution gradually becomes coloured, and the odour of tetranitromethane ultimately disappears. Nitrous fumes are evolved as the reaction proceeds, and the solution becomes acid. If sodium hydroxide is added to the solution at the beginning of the reaction, the decomposition is more satisfactory, and if the solution does not become acid, there is no evolution of nitrous fumes. When the reduction is complete, the solution contains the sodium salt of nitroform, and responds to tests for nitrites and sulphates. Sodium hydroxide is used up in the reaction, and if sufficient is not present the solution becomes acid. The reaction proceeds according to the equation

$$C(NO_2)_4 + Na_2SO_3 + 2NaOH = (NO_2)_3CNa + Na_2SO_4 + NaNO_2 + H_2O.$$

In an actual experiment, 40 grams of sodium sulphite were dissolved in 300 c.c. of water, sodium hydroxide solution being present. Eighteen grams of tetranitromethane were added, and

the mixture was shaken for half an hour. Sodium hydroxide was added at intervals as required. After about an hour, the odour of tetranitromethane had completely disappeared, and the solution was deep orange. No nitroform salt separated out, but, on acidifying with sulphuric acid and extracting with ether, nitroform was obtained. The yield may be ascertained by adding potassium alkyloxide to an aliquot part of the ethereal solution to precipitate the characteristic potassium salt. The yield of potassium salt from the above quantities was 12 grams.

Potassium Sulphite.—The use of this is preferable to sodium sulphite, since the sparingly soluble potassium salt of nitroform is precipitated, and may be isolated by filtration. The solution is liable to become acid during the process, and small quantities of potassium hydroxide solution must be added at intervals. After the experiment, the solution responds to tests for sulphate, and it is therefore evident that the initial strength of the sulphite solution must be such that the less soluble sulphate will not finally be present in quantities sufficient to saturate the solution and crystallise out, contaminating the nitroform salt.

Arsenious Acid.—This proves a very good reducing agent, degrading tetranitromethane to the nitroform salt in a short time. In a typical experiment, 25 grams of arsenious oxide were dissolved in 200 c.c. of water, a sufficient quantity of potassium hydroxide being added. On the addition of 10 grams of tetranitromethane, the yellow nitroform salt separated out after a little vigorous shaking. After a short time, the tetranitromethane was completely decomposed, and 7·8 grams of dry nitroform salt were collected. The crystals so obtained are dull yellow, but, after recrystallisation from water, have the characteristic yellow appearance of the pure salt. The filtrate responds to the usual tests for nitrites and arseniates.

Hydrazine.—Preliminary experiments indicated that tetranitromethane was rapidly acted on by hydrazine, nitrogen being evolved. In an experiment on a larger scale, 20 grams of hydrazine sulphate and 40 grams of potassium hydroxide were added to 500 c.c. of water. Thirty grams of tetranitromethane were then added in small quantities, the mixture being gently shaken in an unstoppered bottle. The potassium salt of nitroform rapidly separated, and the reduction was complete in a quarter of an hour. Twenty-five grams of the dry nitroform salt were collected from this experiment. The reaction proceeds according to the equation

$$NH_2{\cdot}NH_2 + 2C(NO_2)_4 + 4KOH = 2(NO_2)_3CK + 2KNO_2 + N_2 + 4H_2O.$$

It appeared probable that a method for estimating tetranitromethane could be based on this reaction, and it is found that the

method gives results within the limit of experimental error. Half a gram of tetranitromethane is a convenient amount to use, as it liberates some 30 c.c. of nitrogen from hydrazine solutions. As the estimation is carried out in a Lunge nitrometer graduated to 0·2 c.c., the experimental error in reading the volume of gas evolved in the reaction may well be this amount. From the quantitative relation given above, 0·2 c.c. of nitrogen corresponds approximately with 0·0035 gram of tetranitromethane. Using half a gram of the nitro-compound, the error in reading the nitrometer should theoretically be within a margin of 1 per cent. The results obtained are well within this limit.

Phenylhydrazine has been substituted for hydrazine in some observations, but the volume of nitrogen liberated was some three times greater than the calculated quantity. The reduction with this reagent is evidently carried past the nitroform stage, and in actual experiments, phenylhydrazine was found to liberate more than the additional two volumes when it acted on the potassium salt of nitroform.

As hydrazine itself does not attack the nitroform salt, the method can be applied to estimate tetranitromethane in solutions which also contain nitroform, and since the reaction takes place in the presence of excess of potassium hydroxide, it may be used for estimation of solutions containing nitrous and nitric or other mineral acid in addition to the nitro-compound.

In the estimation, a Lunge nitrometer is filled with mercury, as in the Crum method of estimating nitrates. A 10 per cent. solution of tetranitromethane in alcohol is of a convenient strength for use. The nitro-compound was purified by repeated washings with water and by subsequently freezing and melting several times. It was colourless and melted at about 13·4°. The hydrazine solution is prepared by adding 10 grams of hydrazine sulphate and 20 grams of potassium hydroxide to about 80 c.c. of water, filtering, and diluting to 100 c.c. Five c.c. of the freshly prepared hydrazine solution contain an excess of the reagents required by 5 c.c. of the tetranitromethane solution. One c.c. of the hydrazine solution is introduced into the nitrometer, and the last traces are washed in with small quantities of water. This acts as a cushion, which prevents contact of the solution of the nitro-compound with the mercury. Five c.c. of the tetranitromethane solution are now carefully introduced and washed in with alcohol. This solution floats on the top of the hydrazine solution previously introduced, and little reaction takes place. Four more c.c. of the hydrazine solution are now added, and, on falling through the tetranitromethane solution, a reaction rapidly ensues. Nitrogen is quickly

evolved, and the potassium salt of nitroform is precipitated. On account of the rapidity with which the nitrogen is evolved, it is imperative to have the mercury poured out of the side-limb of the nitrometer before the introduction of the hydrazine solution. If this is not done, there is an inevitable loss of nitrogen, as the mercury is driven down quickly, and consequent pressure develops almost immediately. The main reaction is over in less than a minute, but further traces of nitrogen are evolved on shaking once to mix the solutions thoroughly. As the reaction is exothermic, the nitrometer must be allowed to remain for some time before a volume reading is taken.

Sodium hydroxide may be substituted for potassium hydroxide, but the latter is preferable. The following are typical results, obtained at various times by different observers. Five c.c. of a 10 per cent. solution of tetranitromethane in alcohol were taken in each case, and the weights of tetranitromethane in 100 c.c. of solution were found to be: (1) 9·938; (2) 9·904; (3) 9·994; (4) 9·926 grams.

It is therefore evident that the reduction of tetranitromethane by hydrazine is quantitative, and the reaction affords an easy and rapid method for estimating the nitro-compound. Conversely, standard solutions of tetranitromethane may be employed in the estimation of hydrazine in solutions of its salts.

THE CHEMICAL LABORATORIES,
QUEEN'S UNIVERSITY,
BELFAST.

[*Received, May 27th,* 1920.]

THE Council has ordered the following letter and report to be printed in the Journal of the Society:

WHINFIELD,
SALCOMBE,
S. DEVON,
July 10th, 1920.

GENTLEMEN,

I beg to submit the Report of the International Committee on Atomic Weights for 1920–1921, to which I have affixed, by his desire, the signature of Prof. Urbain.

The Report deals with the atomic weights of fluorine, silicon, lead (isotopic), tellurium, scandium, and samarium; and draws attention to the critical work of Guye on the reduction of experimental data, and to the paper of Van Laar on the method of calculating atomic weights.

Certain of the newly published values are confirmatory of those already in use; others are preliminary, and fuller details are promised. The only change at present suggested is in the case of scandium, namely, from 44·1 to 45·1, which appears to be fully justified by the experimental evidence.

I am, Gentlemen,
Your obedient Servant,
T. E. THORPE.

The Hon. Secretaries,
The Chemical Society,
London.

Report of the International Committee on Atomic Weights for 1920–1921.

Since the report of this committee for the preceding year was prepared, only a few new determinations of atomic weights have been published. They may be summarised as follows:

Fluorine.—Moles and Batuecas (*J. Chim. Phys.*, 1919, **17**, 538) have made twenty-three determinations of the density of methyl fluoride, CH_3F. For the weight of a normal litre of the gas, they find, in mean, 1·54542 grams. From this the molecular weight, 34·024, is deduced, and F = 18·996. This, rounded off to 19, is the value already accepted.

Silicon.—Baxter, Weatherill, and Holmes (*J. Amer. Chem. Soc.*, 1920, **42**, 1194), from analyses of silicon tetrachloride, find Si = 28·111. This determination, however, is not regarded by the authors as final. Its acceptance, therefore, must await confirmation, especially as the value is much lower than that given in the present table of atomic weights.

Lead.—The atomic weight of isotopic lead from thorium minerals has been determined by Hönigschmid (*Zeitsch. Elektrochem.*, 1919, **25**, 91). For lead from Norwegian thorite, he finds Pb = 207·88 to 207·92. For lead from Ceylonese thorianite, Pb = 206·88 to 207·24. In thorianite, there is evidently a mixture of isotopes, and perhaps also of normal lead.

Richards and Sameshima (*J. Amer. Chem. Soc.*, 1920, **42**, 929) have examined lead from a radioactive Japanese mineral. The values found for the atomic weight were 207·11, 207·12, and 207·15. For ordinary lead, the corresponding value was 207·184. The Japanese material, evidently, contained very little isotopic lead.

Tin.—In two papers, Brauner and Krepelka (*ibid.*, 917, 928) give new determinations of the atomic weight of tin based upon analyses of the tetrabromide. In the first paper, which is preliminary, they find Sn = 118·70. In the second, by Krepelka alone, the value Sn = 118·699. This confirms the earlier determinations by Briscoe and by Baxter and Starkweather. The work of the last-named chemists appears in full in the same number of the Journal. It was noticed in our last report from a preliminary publication.

Tellurium.—From analyses of the hydride, TeH_2, Bruylants and Michielsen (*Bull. Acad. roy. Belg.*, 1919, Nos. 2—3, 119) find for tellurium the values Te = 127·73, 127·79, and 127·4. The last value they reject. As these determinations are preliminary, they need no further consideration now.

Scandium.—Meyer and Schweig (*Zeitsch. anorg. Chem.*, 1919, **108**, 303), after a study of methods for the purification of their material, give determinations of the atomic weight of scandium by the usual sulphate method. They found Sc = 45·03—45·37, in mean 45·23, but conclude that the method is untrustworthy. Hönigschmid (*Zeitsch. Elektrochem.*, 1919, **25**, 93), with some of the same material, prepared scandium bromide and determined its ratio to silver. In eighteen concordant analyses, he found Sc = 45·099, which may be rounded off to 45·1. This value is accepted by Meyer and Schweig, and should be adopted.

Samarium.—The atomic weight of samarium has been determined by Owens, Balke, and Kremers (*J. Amer. Chem. Soc.*, 1920, **42**, 515) by analyses of the anhydrous chloride. From the mean of eighteen concordant analyses, Sa = 150·43, in close agreement with

the determinations by Stewart and James, 150·44, which was noticed in our report of last year.

Apart from the actual determination of atomic weights, three papers relative to the reduction of the experimental data deserve attention. Guye (*J. Chim. Phys.*, 1919, **17**, 171), in one paper, has discussed the application of Avogadro's law to this problem. In a second paper (*ibid.*, 141), he has examined the data relative to bromine and silver, and concludes that Br=79·92 and Ag=107·87. The last figure differs from the value 107·88, as given in the table, by only 0·01, which is quite within the limits of experimental uncertainty. The third paper, by Van Laar (*ibid.*, 266), relates to the method of calculating atomic weights.

The only change in the table of atomic weights is in the case of scandium—from 44·1 to 45·1—which appears to be fully justified by the evidence.

(*Signed*) F. W. Clarke.
T. E. Thorpe.
G. Urbain.

1921.

International Atomic Weights.

	Symbol.	Atomic weight.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	10·9
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·005
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·1
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	70·1
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·00
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·20
Lithium	Li	6·94
Lutecium	Lu	175·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (radium emanation)	Nt	222·4
Nitrogen	N	14·008
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·9
Radium	Ra	226·0
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	45·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·06
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·15
Thulium	Tm	168·5
Tin	Sn	118·7
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·2
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	173·5
Yttrium	Yt	89·33
Zinc	Zn	65·37
Zirconium	Zr	90·6

C.—*Organic Derivatives of Tellurium. Part II. Constitution of the Dimethyltelluronium Dihaloids.*

By Richard Henry Vernon.

In Part I (this vol., p. 86), the isomerism of the dimethyltelluronium dihaloids of the type $TeMe_2X_2$ was established.

It was likewise shown that there were two bases, the α and the β, and that the latter was obtained by evaporating (under specified conditions) an aqueous solution of the former to complete dryness.

Direct analyses of pure samples of the β-base have confirmed the supposition that it was dimethyltelluronium oxide, $TeMe_2O$.

Analysis of the α-base is out of the question, since investigation has shown that it can only exist as such in the presence of an excess of water. If this excess is gradually removed by evaporation, there is a gradual transition from the α- to the β-form, and it will be proved in the experimental part that complete conversion is accompanied by the loss of water; and that, furthermore, the relationship existing between the two bases is expressed by the equation:

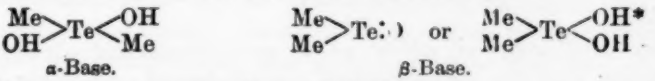
$$\underset{\beta\text{-Base.}}{TeMe_2O} + H_2O = \underset{\alpha\text{-Base.}}{[TeMe_2O],H_2O}.$$

If the α-base had the indicated constitution, it would give the β-dihaloids on treatment with halogen acids and not the α. It must, therefore, be a dimethyltelluronium dihydroxide, $TeMe_2(OH)_2$.

That two bases, $TeMe_2O$ and $TeMe_2(OH)_2$, give totally different isomeric halogen derivatives can be explained by assuming that the radicles in the two bases are differently arranged around the tellurium atom, and since in the β-base two valencies of the tellurium are directly connected with an oxygen atom, it is reasonable to suppose that the corresponding haloids have the halogens (and hence the methyl groups) in proximity to each other.

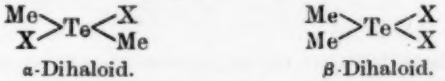
In short, the β-dihaloids have a *cis*-constitution, and the above hypothesis leads to a *trans*-constitution for the α.

The constitution of the two bases is therefore



α-Base. β-Base.

and that of the corresponding dihaloids



α-Dihaloid. β-Dihaloid.

* It is quite immaterial whether the β-base be written as a dihydroxide, $TeMe_2(OH)_2$, or as the oxide, $TeMe_2O$, provided its *cis*-constitution is indicated.

Some interesting observations were made during the investigation of methyl telluride, which was prepared for the first time in a state of purity.

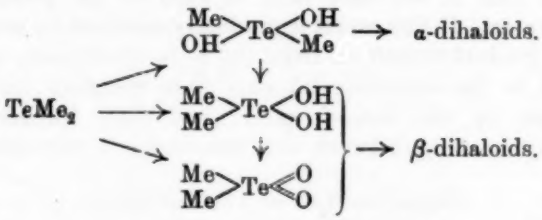
The position of the methyl groups in methyl telluride must be the same as their position in the α-dihaloids because methyl telluride directly unites with the halogens according to the equation

$$TeMe_2 + X_2 = TeMe_2X_2,$$

giving the corresponding α-dihaloids but never the β.

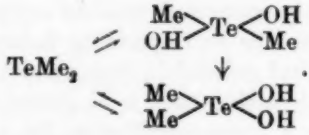
According to the extent of oxidation of methyl telluride with hydrogen peroxide, either the α- or the β-base can be obtained.

The α-base can be directly oxidised to *dimethyltellurone*, $TeMe_2O_2$, through the intermediary of the β-base, and another intimate relationship existing between these substances can be expressed by the scheme:



As is to be expected, the tellurone also gives β-dihaloids with halogen acids.

Since methyl telluride can be obtained by the dry distillation of either the α-* or β-base, by reduction of an α-dihaloid, or from a β-dihaloid by conversion into the base and subsequent dry distillation of the latter, there exists a regular reversible cycle between the two bases and methyl telluride.



The direct transition from the β- to the α-base is, however, not possible.

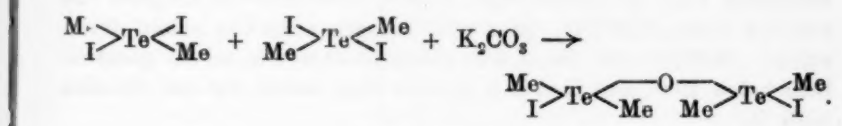
Dry distillation of either an α- or a β-dihaloid always gives tellurium and the corresponding methyl haloid, according to the equation:

$$TeMe_2X_2 = Te + 2MeX,$$

* It should be noted that the α-base consists of the β-base plus water, $TeMe_2(OH)_2 = TeMe_2O + H_2O$; hence if the β-base gives methyl telluride on dry distillation, so does the α.

and, although but little insight into the constitution of these substances is gained, the experiment indicates (but does not establish) the equivalence of the four tellurium valencies. If the four valencies were not equivalent, the dry distillation of one series of dihaloids would probably give different products of decomposition from that of the other.

The most remarkable difference between the α- and the β-dihaloids is their behaviour towards alkali hydroxides or carbonates. Thus the α-di-iodide and potassium carbonate give di-iodotetramethylditelluronium oxide, $Te_2Me_4I_2O$.



On the other hand, the β-di-iodide and potassium carbonate give trimethyltelluronium iodide, $TeMe_3I$.

Since trimethyltelluronium iodide can also be prepared from the α-di-iodide, it follows that both α- and β-dihaloids give the same trimethyltelluronium haloids. The *cis*-position of the methyl radicles in the β-dihaloids militates against their stability, and they are inclined to wander. This has been observed repeatedly, and is in marked contrast to the great stability of the methyl groups in α-derivatives. No wandering of methyl groups in an α-dihaloid has ever been noticed.

The wandering and general instability of the methyl groups in the β-dihaloids has made it impossible to prepare other derivatives than the dihaloids.

Normal salts of the α-series can be prepared in any number and without the slightest difficulty. As an example, the α-benzoate prepared by the interaction of the α-di-iodide and silver benzoate has already been mentioned in Part I. All attempts to prepare the corresponding β-benzoate resulted in an amorphous powder of indeterminate composition.

The general behaviour of the β-dihaloids indicates that the *cis*-position of the methyl groups is not conducive to their stability, and the whole molecule appears to be in a state of strain.

The *trans*-position is the normal and stable one, as is evident by the perfectly normal behaviour of the α-series.

The designation of the two series by the letters α and β will be adhered to, since these prefixes are simpler than "cis" and "trans," and the dimethyltelluronium dihaloids, considered as a whole, will be referred to as "dihaloids" or "haloids" for short.

Experimental.

Methyl Telluride.

The first mention in the literature of methyl telluride, $TeMe_2$, is by Wöhler and Dean (*Annalen*, 1855, **93**, 233), who obtained a dark brown oil by the action of barium methyl sulphate on potassium telluride.

This oil was not investigated as such, but the conclusion that it was methyl telluride was drawn from indirect evidence; for on treatment with nitric acid, the nitrate, to which was assigned the formula $TeMe_2O,2HNO_3$, gave with halogen acids the haloid derivatives. Wöhler and Dean also mention that the oil in question boils below 100°, and that it is heavier than water, but not miscible with it.

Attempts to prepare methyl telluride by this method invariably gave a black tarry mass, and although the nitrate, and hence the haloids, could be obtained, methyl telluride as such could not be isolated.

Another experiment, using methyl sulphate and potassium telluride, gave an oil containing sulphur which was not further investigated. The interaction between methyl iodide and potassium telluride gave a negative result.

It was at length found that methyl telluride could be prepared by the reduction of Demarçay's iodide with sodium sulphite in the presence of sodium carbonate. Other reducing agents invariably reduced the di-iodide to tellurium.

An excellent yield of methyl telluride is obtained according to the equation:

$$\underset{(\alpha.)}{TeMe_2I_2} + H_2O + Na_2SO_3 = Na_2SO_4 + 2HI + TeMe_2,$$

$$2HI + Na_2CO_3 = 2NaI + CO_2 + H_2O.$$

To a solution of 13 grams of sodium sulphite (hydrated) and 6 grams of sodium carbonate in 200 c.c. of water contained in a 500 c.c. distilling flask connected with a long, water-cooled condenser, 20 grams of the α-iodide are added. The flask is gently warmed, the iodide rapidly dissolved, and an emulsion results. The temperature is slowly raised and the telluride passes over rapidly at about 75°; most of it will have distilled over before the solution begins to boil. A few minutes' boiling will suffice.

The pale yellow or brown oil is separated from water, kept overnight with anhydrous sodium sulphate, and fractionated, when it distils at 94°/770 mm.

Methyl telluride is a very pale yellow oil which solidifies in liquid air, but not in carbon dioxide and ether, is somewhat heavier than water, and possesses the most abominable and persistent odour of all tellurium compounds (Found: C = 15·22; H = 3·85. Calc.: C = 15·24; H = 3·80 per cent.). The boiling point of methyl telluride completes the list of boiling points of the dimethyl derivatives of the sixth group of the periodic system. These are: Me_2O −23°, Me_2S 37°, Me_2Se 58°, and Me_2Te 94°.

Methyl telluride dissolves slowly in water, and the aqueous solution does not contain the telluride as such, but is a solution of the α-base. This is shown by its alkalinity and the potassium iodide test.* The reaction between the telluride and water is probably $TeMe_2 + H_2O + O = TeMe_2(OH)_2$, the oxygen being derived from the atmosphere.

If hydrochloric acid is added to an emulsion of the telluride in water, the solution gives a positive α-iodide test, the red precipitate increasing on keeping, and being especially noticeable on the surface of the liquid, where contact with the air is maintained. The addition of a trace of an oxidising agent, such as potassium permanganate, sodium hypochlorite, etc., instantly precipitates the whole of the α-iodide. This reaction is simply due to the oxidation of the methyl telluride to the α-base, which, in its turn, gives the α-dihaloid.

The action of oxidising agents, and especially of hydrogen peroxide, is of interest, since either base, and in consequence either α- or β-haloids can be obtained.

If just sufficient hydrogen peroxide is added completely to dissolve the telluride on slightly warming, an alkaline solution is obtained which gives the usual tests for the α-base.

$$TeMe_2 + H_2O_2 = TeMe_2(OH)_2.$$

If an excess of hydrogen peroxide is used, and the solution boiled for a short time, the telluride is oxidised to the β-base, from which the β-dihaloid can be prepared.

$$TeMe_2 + O = TeMe_2O.$$

Prolonged boiling of the telluride with an excess of peroxide eventually produces a turbidity and a gradual precipitation of a pure white, amorphous powder. This, as will be shown, is the tellurone, $TeMe_2 + O_2 = TeMe_2O_2$.

A confirmation of these results consists in directly oxidising pre-

* A simple test to distinguish the two bases is to acidify them with hydrochloric acid, and then add a concentrated solution of potassium iodide. The α-base is indicated by a bright yellow precipitate which rapidly becomes brick-red (α-di-iodide). The β-base instantly gives a deep blood-red precipitate (β-di-iodide) without the preliminary yellow phase.

parations of the two bases, the tellurone resulting in each case.

The action of sodium hypochlorite on the telluride is similar to the combined action of hydrogen peroxide and hydrochloric acid. Either α- or β-dichlorides are obtained.

An acid solution of potassium permanganate probably acts in the same way, and the vapour of methyl telluride is completely absorbed by a bubbler containing a 5 per cent. solution.

A fairly delicate test for the presence of methyl telluride vapour is to bubble it through concentrated sulphuric acid. This at first becomes a delicate pink, but is subsequently decolorised.

Methyl telluride deposits colourless crystals on keeping, and, although their composition is not known, they are probably some oxidation product of the telluride (β-base ?).

Dimethyltellurone.

As already mentioned, the tellurone can be obtained by oxidation either of methyl telluride, or of either of the two bases.

The best method of preparing the tellurone is to evaporate on the water-bath a solution of the α-base with an excess of hydrogen peroxide. The oxidation of the α-base appears to take place more readily than that of the β-base, but it is quite immaterial which is used. The white, amorphous powder is collected, washed with water and alcohol, and then dried. On account of its insolubility in all solvents, it cannot be further purified, and the analytical figures are not in close agreement. (Found: C = 10·50; H = 3·19. $C_2H_6O_2Te$ requires C = 12·60; H = 3·20 per cent.) This substance possesses all the characteristics of the peroxides; thus it oxidises the halogen acids to the corresponding halogen, decolorises potassium permanganate, and has explosive properties.

Trimethyltelluronium Iodide.

Trimethyltelluronium haloids, $TeMe_3X$, were first mentioned by Cahours (*Compt. rend.*, 1865, **60**, 624), and later on Scott describes the preparation of trimethyltelluronium iodide from the α- or Demarçay's iodide (P., 1904, **20**, 157).

Trimethyltelluronium iodide is of great interest from a theoretical point of view, since it can be prepared directly from either of the two di-iodides.

Its preparation from the α-di-iodide consists in reducing the latter and then treating the methyl telluride with methyl iodide. The reaction is violent, heat is evolved, and it is advisable to dilute the telluride with some solvent like chloroform, etc. On gently

warming, the colourless, crystalline iodide is deposited. Scott prepared it directly by treating the α-di-iodide with sodium sulphite and methyl iodide.

Trimethyltelluronium iodide crystallises in colourless, fibrous needles. It has no definite melting point, and decomposes on heating. It is very readily soluble in water, and crystallises well from this solvent. (Found: I = 42·20. Calc.: I = 42·40 per cent.)

To prepare the compound from the β-di-iodide, it is only necessary to boil two molecular proportions of the latter with one molecular proportion of a concentrated aqueous solution of sodium carbonate. The colourless solution deposits the fibrous crystals on cooling, and these are recrystallised from water until their solution no longer gives a red precipitate with hydrochloric acid.

Although the mechanism of the formation of trimethyltelluronium iodide from the β-di-iodide is not clear, the obvious wandering of the methyl groups is somewhat reminiscent of the sulphonium compounds.

No explanation of this reaction will be attempted, but in view of its curious and unexpected nature, the salt was analysed. (Found: C = 12·03; H = 3·14; I = 42·34. Calc.: C = 12·00; H = 3·00; I = 42·40 per cent.)

If a methyl-alcoholic solution of the β-di-iodide is titrated until decolorisation with, for example, sodium hydroxide, one molecule of alkali is required for one molecule of the iodide (Found: 100 grams required 9·13 NaOH. Calc.: 9·73 grams).

With an alkali carbonate, one molecule is required for two of the iodide (Found: 100 grams required 12·15 Na_2CO_3. Calc.: 12·89 grams). This experiment indicated, therefore, the ratio of sodium carbonate to β-di-iodide necessary for the above preparation.

The totally different behaviour of the α-iodide towards the alkalis will be dealt with in a separate paper.

The β-Base.

Owing to the extremely hygroscopic nature of this base and its complete decomposition at relatively low temperatures, considerable difficulty attended the preparation of a pure specimen for analytical purposes. The following method was eventually adopted.

The discoloured base obtained from 24 grams of the α-di-iodide (*loc. cit.*, p. 93) is redissolved in water, and the solution, after filtration, is evaporated to dryness at a temperature not exceeding 70° (10—20 mm. pressure), and this operation is repeated until a colourless preparation is obtained.

A boat containing the base is placed in a small weighing bottle with a ground glass stopper. This is held in a glass tube, closed

at one end, and connecting at the other through a set of calcium chloride tubes to a good water-pump. A bath containing boiling chloroform keeps the base at a constant temperature. After about ten hours, the weighing bottle is removed, weighed, and the boat instantly transferred to the combustion tube. The base cannot be dried to constant weight as it is slightly volatile (Found: C = 13·26; H = 3·45. Calc.: C = 13·83; H = 3·46 per cent.).

Distillation of the β-Base.—On heating, the base begins to decompose at about 100° at atmospheric pressure, and at 80—90° under diminished pressure.

The apparatus used in these experiments consisted of a 50 c.c. distilling flask connected to a suitably constructed receiver. The flask was heated by a sulphuric acid-bath, and the receiver was thoroughly cooled in a mixture of carbon dioxide and ether. On slowly raising the temperature, the base melts, swells enormously to a dry, powdery, brown mass, and a liquid condenses in the receiver. As a rule, the residue remaining in the distilling flask amounts to about 45 per cent. and the distillate to about 51 per cent. of the weight of base taken.

As the weight of the residue plus the weight of the distillate was never exactly equal to the weight of the base, it became necessary to ascertain whether this was due to experimental error or to some gas that was evolved during the distillation.

That the latter is not the case was shown by connecting the receiver with a eudiometer filled with mercury, and after completion of the distillation it was found that the volume of gas collected corresponded very exactly with the calculated volume of air displaced. This was confirmed by connecting the receiver through a complicated set of drying tubes with a combustion tube filled with copper oxide and kept at a red heat. No evidence of the formation of carbon dioxide or water was obtained.

Analysis of the brown residue remaining in the distilling flask showed it to be of somewhat indefinite composition. Analytical figures approximated fairly closely, however, with a compound or mixture of the type $Te_2Me_2O_2$ (Found: C = 7·60; H = 1·92. Calc.; C = 7·56; H = 1·80 per cent.).

The distillate, which passes over at about 86° under normal pressure, usually, but not invariably, consists of two layers, which are still liquid in carbon dioxide and ether. On drying this obvious mixture with anhydrous sodium sulphate, and fractionating, the upper and colourless layer passes over at 62°, and the lower and faintly yellow layer at 94°. The boiling point of 94°, and analysis of the trimethyltelluronium iodide obtained with methyl iodide, showed that this fraction was methyl telluride.

The first fraction was not further investigated, owing to the intolerable nature of these substances.

There is good reason to presume, however, that it is dimethyltelluronium dimethoxide, $TeMe_2(OMe)_2$, and the decomposition of the base on dry distillation could be expressed somewhat as follows:

$$4TeMe_2O = TeMe_2 + TeMe_2(OMe)_2 + Te_2Me_2O_2.$$

The α-Base.

If an aqueous solution of the α-base is slowly evaporated on a water-bath or in a vacuum desiccator, potassium iodide tests taken at intervals show the unaltered α-base until a certain point is reached. If the evaporation is continued still further, the presence of the β-base is at once observed.

The point at which the α- begins to change into the β-base occurs when colourless, deliquescent crystals make their first appearance in the solution.

The loss of water between the point of transition and complete conversion of the α- into the β-base corresponds closely with one molecule, and in consequence the α-base must be dimethyltelluronium dihydroxide, $TeMe_2(OH)_2$.

The composition of the α-base was determined as follows: 5·6350 grams of a somewhat syrupy solution of the base were placed in a weighed U-tube, one limb of which was sealed and the other connected with a calcium chloride tube. This in its turn communicated through a set of drying tubes to a good water-pump.

The dehydration of the syrup was effected at 70° (boiling chloroform) under 12 mm. pressure.

Potassium iodide tests were taken every hour, and the first indication of the β-base occurred after an interval of six hours, the weight of α-base and water being reduced from 5·6350 to 2·6886 grams. The calcium chloride tube was then weighed, and the dehydration continued until its weight remained constant. The increase in weight was 0·2342 gram, and the residue (β-base) in the U-tube weighed 2·3988 grams. Hence 100 grams of the α-base lose 8·7 grams of water, leaving 89 grams of the β-base.

The equation $TeMe_2(OH)_2 = TeMe_2O + H_2O$ requires 9·2 grams of water and 90·8 grams of the β-base.

In view of experimental difficulties, the agreement is reasonably good.

Dry Distillation of the α- and β-Dihaloids.

A dry distillation of the β-di-iodide, conducted in precisely the same manner as that of the α-di-iodide (*loc. cit.*, p. 91), gave

MeI = 66; Te = 34 (Calc.: MeI = 69; Te = 31 per cent.). A similar experiment with the β-dibromide gave MeBr = 58; Te = 42 (Calc.: MeBr = 59; Te = 41 per cent.).

An experiment showing the decomposition of any one of the six dihaloids, according to the general equation

$$TeMe_2X_2 = Te + 2MeX$$

can be made by sealing up the dihaloid in a small glass tube, one end of which is drawn out into a fine point. The tube is then bent at right angles, and the dihaloid in the rounded end carefully heated. The liquid methyl haloid will condense in the pointed end of the tube, and amorphous tellurium will be found in the other.

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CI.—*Volumetric Estimation of ββ′-Dichloroethyl Sulphide.*

By WILLIAM FRANCIS HOLLELY.

THE usual procedure for the estimation of ββ′-dichloroethyl sulphide in "mustard gas" is to distil a known volume of the sample under diminished pressure and to collect the fraction boiling at 125—130°/40 mm. This product is fairly pure ββ′-dichloroethyl sulphide, melting at about 10°, and the volume obtained affords an approximation of the purity of the crude product.

This procedure involves personal risks, and gives no accurate figure for the absolute percentage of ββ′-dichloroethyl sulphide, as the latter fraction also contains higher chlorinated compounds and other impurities.

With the object of overcoming these difficulties, the following volumetric method for the estimation of ββ′-dichloroethyl sulphide in "mustard gas," with or without solvents, has been devised; it depends on the fact that ββ′-dichloroethyl sulphide forms a definite double salt with cuprous chloride, of the constitution,

$$[(CH_2Cl{\cdot}CH_2)_2S]_2Cu_2Cl_2.$$

As the higher chlorinated compounds do not react with cuprous chloride, the method is applicable for the absolute estimation of ββ′-dichloroethyl sulphide.

Procedure.—About 1 gram of the sample is weighed into a stoppered 100 c.c. conical flask, and to this 10 c.c. of a standardised solution of cuprous chloride in absolute alcoholic hydrogen chloride is added from a burette.

The cuprous chloride solution should only be prepared immediately before use. The best means to adopt is to have a 10 per cent. solution of hydrogen chloride in absolute alcohol on hand, and to dissolve 5 grams of pure cuprous chloride in 50 c.c. of it when required.

The "mustard gas" sample readily dissolves in the alcoholic solution, and the contents of the flask are allowed to remain for ten minutes in the cold, with occasional rotation. At the end of this time, the whole is gradually diluted with careful agitation and cooling in water, by the addition of 50 c.c. of a 5 per cent. aqueous sodium chloride solution from a burette.

After the addition of about 3 c.c. of the diluent, the contents of the flask become semi-solid owing to the partial precipitation of the cuprous chloride double salt, in the form of fine colourless needles; it is advisable to allow this to occur as it hastens the complete precipitation of the double salt in a crystalline condition on total dilution, whilst the excess of cuprous chloride is held in solution by the sodium chloride.

On total dilution, the contents of the flask are well mixed by careful shaking, allowed to remain for a minute or two, and the liquid is then filtered from the precipitate through glass wool into a dry burette. The filtrate is quite clear, and the amount of copper in a known volume of it is subsequently determined in terms of c.c. of $N/10$-sodium thiosulphate, by the titration of iodine liberated from potassium iodide.

It is impracticable to wash the double salt free from the excess of cuprous chloride, as it dissociates to some extent in contact with water. This difficulty is overcome by knowing the total volume of the 10 c.c. of standard cuprous chloride solution, plus the 50 c.c. of diluent, which is found to be 59·5 c.c. By this means the total excess of cuprous chloride is readily calculated from the amount contained in the known volume of the filtrate taken for the copper estimation.

Estimation of the Copper.—Usually 30 c.c. of the filtrate are run from the burette into a 250 c.c. conical flask and 5 c.c. of hydrogen peroxide (20 per cent. by volume) are added while cold to oxidise the copper to the cupric form. The contents of the flask are then gently boiled nearly to dryness, which operation is repeated twice after the addition of 10 c.c. of water to ensure that traces of gaseous oxidising agents are removed. The residue is

diluted with 50 c.c. of water and sodium carbonate solution added to give a slight precipitate, which is redissolved by the careful addition of dilute acetic acid. A slight excess of potassium iodide is added, and the liberated iodine is titrated in the usual way with $N/10$-sodium thiosulphate. Together with this, the original alcoholic cuprous chloride solution is standardised in terms of c.c. of $N/10$-thiosulphate by oxidising 5 or 10 c.c. with hydrogen peroxide, and subsequently treating as already detailed.

From the results of these titrations, the percentage of $\beta\beta'$-dichloroethyl sulphide is readily determined.

The formula of the double salt being $[(CH_2Cl\cdot CH_2)_2S]_2Cu_2Cl_2$, 127 grams of copper correspond with 318 grams of $\beta\beta'$-dichloroethyl sulphide. As 1 c.c. of $N/10$-thiosulphate corresponds with 0·00635 gram of copper, therefore 1 c.c. of $N/10$-thiosulphate = 0·0159 gram of $\beta\beta'$-dichloroethyl sulphide, the percentage of which $= \frac{(A-B)\times 0{\cdot}0159\times 100}{\text{Weight of sample}}$, where A = c.c. of $N/10$-thiosulphate corresponding with copper in the 10 c.c. of standard cuprous chloride solution, and B = c.c. of $N/10$-thiosulphate corresponding with copper in the 59·5 c.c. of filtrate, that is, the total excess of copper.

The following table gives some results obtained with different samples of "mustard gas" compared with those given by the distillation method:

Sample.	Weight taken. Grams.	C.c. of $N/10$-thiosulphate. A.	C.c. of $N/10$-thiosulphate. B.	$\beta\beta'$-Dichloroethyl sulphide. Per cent. Titration.	$\beta\beta'$-Dichloroethyl sulphide. Per cent. Distillation.
I.....	0·9908	101·2	39·5	99·0	
	0·9617	100·2	40·4	98·5	100
	0·9032	100·2	44·0	98·9	
II.....	1·3000	127·0	49·2	95·1	100
	1·0822	106·4	41·6	95·2	
III.	1·2824	99·0	42·40	70·2	76
	1·3398	99·0	40·4	69·6	
IV.....	1·2642	99·0	49·6	62·1	65
	0·9166	106·4	70·8	61·7	

Sample I was specially pure $\beta\beta'$-dichloroethyl sulphide, obtained after three redistillations, freezing, and draining off the residual liquid. It melted at 13·5°.

Sample II.—Once distilled $\beta\beta'$-dichloroethyl sulphide from crude product. M. p. 12·5°.

Sample III.—Crude product as manufactured. M. p. 8°.

Sample IV.—Crude product + solvent. M. p. −3°.

Higher Chlorinated Compounds and Cuprous Chloride.

Equal volumes of 95 per cent. ββ′-dichloroethyl sulphide and sulphur monochloride were mixed and allowed to remain at the ordinary temperature for two weeks. Hydrogen chloride was evolved and sulphur separated, showing that some chlorination had taken place. The product was then distilled, no sulphur monochloride being obtained, and the fraction boiling at 118—120°/20 mm. was reserved. This fraction did not freeze even at −7°; therefore, the greater proportion of the fraction is composed of higher chloro-compounds, although undoubtedly some ββ′-dichloroethyl sulphide was present owing to the difficulty of separating it by fractional distillation.

The following results were obtained by the volumetric method:

(*a*) 1·3172 Grams, using 10 c.c. of alcoholic cuprous chloride (=102 c.c. of *N*/10-thiosulphate), required 67·8 c.c. of *N*/10-thiosulphate for total excess copper. Percentage of ββ′-dichloroethyl sulphide $=\frac{34{\cdot}2 \times 1{\cdot}59}{1{\cdot}3172}=41{\cdot}3$.

(*b*) 1·0804 Grams required 73·7 c.c. of *N*/10-thiosulphate for total excess copper. Percentage of ββ′-dichloroethyl sulphide =41·6.

The sample, after treatment with alcoholic cuprous chloride and dilution, was precipitated as an oily layer, instead of the usual crystalline precipitate. This oily layer, on keeping, gradually became pasty, owing to the separation from its solution of some of the ββ′-dichloroethyl sulphide–cuprous chloride double salt. This qualitative observation, together with the above results which show a fall in the percentage of ββ′-dichloroethyl sulphide from 95 to 41 per cent. after chlorination, indicate that the higher chloro-compounds of ethyl sulphide do not enter into the reaction during this volumetric estimation, no copper salts of these compounds being formed.

Analysis and Properties of the ββ′-Dichloroethyl Sulphide–Cuprous Chloride Double Salt.

The salt was prepared by the method already described, washed with alcohol, and dried in a vacuum, when colourless needles were obtained.

A known weight of the sample was carefully heated with a little concentrated nitric acid to dryness, a few c.c. of water were added, and evaporated. The copper was estimated as usual by potassium iodide and *N*/10-thiosulphate (Found: Cu=24·3, 24·1. $C_8H_{16}Cl_6S_2Cu_2$ requires Cu=24·6 per cent.).

The double salt can be obtained by a variety of means; for example, by stirring the dry components together followed by alcoholic extraction; by shaking the liquid with cuprous chloride solution in dilute hydrochloric acid, and also by the method employed in its detailed estimation. This method is by far the preferable, as it gives a quantitative yield of a crystalline product. The salt readily dissociates on warming with ether, carbon tetrachloride, etc., but less readily in alcohol, when cuprous chloride is precipitated. When heated in water, it readily melts, but dissociation is not rapid, and the salt is insoluble. When stirred with cold ammonium chloride solution or concentrated hydrochloric acid, the salt becomes pasty, owing to partial dissociation and solution of cuprous chloride in the liquid, leaving a proportion of the liquid dichloro-compound.

The crystals have a dissociation or decomposition point rather than a melting point, which occurs at about 60°.

The solubility in various solvents is difficult to judge, owing to the more or less rapid dissociation. The salt can, however, be crystallised from hot alcohol, in which it is fairly soluble, separating in colourless needles, but the solution has to be filtered from some dissociated cuprous chloride.

The vesicant power of the salt appears to be of the same degree as ββ′-dichloroethyl sulphide itself.

General Remarks.—In the estimation of the crude product, with or without solvent, owing to the presence of higher chloro-compounds or solvent, the salt, on being precipitated from the alcoholic solution, contains some lumpy particles, due to the precipitated oily higher chloro-compounds or solvent dissolving some of the double salt. It has been proved quantitatively that these small lumps do not retain any unused cuprous chloride which should pass into solution with the sodium chloride, and the result is not affected.

This volumetric method for the estimation of ββ′-dichloroethyl sulphide has distinct advantages over the distillation method, which does not yield ββ′-dichloroethyl sulphide free from impurities, in that it is a much cleaner process and the personal risk is almost entirely eliminated. Moreover, it is a quick method, as an estimation can be done in less than an hour.

This paper is the result of work carried out at H.M. Factory, Avonmouth, and it is published with the sanction of the Chemical Warfare Department.

67 Ross Road,
Wallington, Surrey. [*Received, June 5th*, 1920.]

CII.—*The Ignition of Gases. Part I. Ignition by the Impulsive Electrical Discharge. Mixtures of Methane and Air.*

By Richard Vernon Wheeler.

The research to which the present paper forms an introduction originated in a desire to obtain information regarding the mechanism of ignition, particularly by electrical means, of mixtures of methane and air. For it is necessary to know with certainty the conditions under which ignition of such mixtures is to be apprehended in coal-mining practice.

As the work progressed, it became apparent that the information required could not be obtained if attention was confined to methane as the inflammable gas in admixture with air, but that it would be necessary to study also the ignition of other members of the paraffin series of hydrocarbons, and of hydrogen, when mixed with air, and of methane when mixed with pure oxygen and with various mixtures of oxygen and nitrogen.

The research, so far as it has progressed, can conveniently be divided under three heads: I, Ignition by heated surfaces; II, ignition by the secondary discharge (high-tension sparks), and III, ignition by electric "break-flashes" (low-tension sparks). These can be subdivided to treat separately under heading I of: (*A*) Ignition by the heated walls of a containing vessel, and (*B*) ignition by hot wires. Under heading II can be grouped the ignition of: (*A*) Mixtures of methane and air; (*B*) mixtures of hydrogen and of different members of the paraffin series of hydrocarbons with air; (*C*) mixtures of methane with oxygen and with mixtures of oxygen and nitrogen. Under heading III the effects will be considered of: (*A*) The inductance of the circuit; (*B*) the rate of break of circuit; (*C*) the materials of the poles; and (*D*) the use of alternating current. It is proposed to submit separate accounts of each of these parts of the research to the Society, not necessarily in the order indicated above, as opportunity affords to prepare the results for publication.

The requisite for a source of heat to initiate flame in a gaseous mixture is that sufficient energy shall be introduced to maintain for a sufficient length of time a sufficient volume of the mixture at or above its ignition-temperature.

Sufficiency of the source of heat will depend on (*a*) the ignition-temperature of the mixture, and (*b*) the specific heats of the mixed

gases. Sufficiency of time will depend on (*c*) the duration of the pre-flame period for the mixture, (*d*) the initial speed of propagation of flame therein, and (*e*) its thermal conductivity. Sufficiency of volume of mixture ignited will depend on (*f*) the thermal value of the reaction.

It will be seen that several of these factors are interdependent. Thus, the ignition-temperature of the mixture and the duration of the pre-flame period both depend on the rate of reaction of the combining gases; whilst the initial speed of propagation of flame in the mixture also depends on the rate of reaction, as well as on its thermal value.

Although this research deals in general with the mechanism of ignition of inflammable mixtures whatever the means employed to effect that ignition, the characteristics of the igniting agent must be considered, if not completely defined. For, by the use of several kinds of igniting agents, each with different known characteristics, the importance to be attached to one or other of the many factors which determine whether or no flame shall be produced in an inflammable mixture can be gauged. Unfortunately, the amount of information available regarding the characteristics of electric discharges is very meagre.

The igniting agent employed for the series of experiments described in this paper was the high-tension spark produced at a gap in the secondary circuit of an induction coil when a current in the primary circuit was broken. When such a spark is examined in a rotating mirror or photographed on a rapidly moving film, it is found to consist of an initial bright spark followed by others of less intensity or by a striated luminous band indicating an undulatory unidirectional discharge. The initial bright spark has the characteristic appearance of a single discharge from a condenser.

According to Morgan ("Principles of Electric Spark Ignition in Internal Combustion Engines," London, 1920), the most important consideration regarding secondary discharges is that each discharge consists of two successive phases, namely, a "capacity component" and an "inductance component." The former corresponds with the spark obtained by the discharge of electrostatic energy from a condenser, the latter with the discharge of electromagnetic energy from a coil. The duration of the capacity component of the secondary discharge is always extremely short, but the value of the current reached in it is much higher than that of the current in the inductance component. The capacity component can be intensified at the expense of the inductance component by increasing the capacity associated with the spark-gap circuit, and it is then found that the igniting-power of

the spark is increased (although its total energy has not been altered). This suggests that when ignition of inflammable mixtures is caused by the secondary discharge, the effective part of that discharge is the capacity component. Paterson and Campbell (*Proc. Physical Soc.*, 1919, **31**, 193) so far share Morgan's views as to suggest that the igniting-power of the discharge is determined by the quantity of electricity in the first spark that passes.

We can, then, characterise the secondary discharge from an induction coil, in relation to its ability to ignite inflammable mixtures, as of exceedingly short duration and high intensity, assuming, with Morgan, that the "capacity component" of the discharge is the effective portion.

For an igniting source of these characteristics, the relative "ignitibilities" of mixtures of methane and air are shown in Fig. 3 (Curve *A*). In this diagram, percentages of methane, over a wide range, are plotted against "igniting-currents"; that is to say, the currents in the primary circuit of an induction coil, which, when broken at a constant rate, induced secondary discharges, at a fixed spark-gap, just capable of igniting the mixtures.

When, as in these experiments, the gap is formed by sharply pointed electrodes, and the voltage is applied with great suddenness (as is the case with an induction-coil), the sparking voltage for a gap of constant width follows, over a wide range, a straight line relationship with the primary current. The energy-content of the "capacity component" of the discharge is $\frac{1}{2}CV^2$, where C is the capacity associated with the gap circuit (including that of the secondary winding) and V is the sparking voltage. Assuming that ignition depends on the energy of the capacity component (and the best available evidence is in accordance with this assumption), it is rational to co-ordinate i^2 (primary current) with percentage of inflammable gas in the mixture. The general character of the curve will not be altered by plotting i, instead of i^2, against percentage.

For our present purpose, it is sufficient to define the induction-coil used for the experiments as an "8-inch" coil of the *X*-ray type. The "trembler" of the coil was removed and direct connexion made between the leads of the primary circuit and a battery of accumulators. Included in the circuit was a contact-breaker of the type previously described (T., 1917, **111**, 130), a regulating resistance, and a Weston A.C. ammeter. The last-named was short-circuited whenever a discharge was passed at the spark-gap, a non-inductive resistance equal to its resistance being included in the circuit in its stead. In some of the earlier series of experiments, a capacity (of 0·25 microfarad) was inserted across the

terminals of the mechanical circuit-breaker to reduce sparking on break, and thus avoid oxidation of the polished steel contacts. To obtain consistent results, it was essential that these contacts should remain clean, and, when currents of much more than 1 ampere were broken, the presence of the capacity aided considerably in maintaining their cleanliness. Duplicate experiments showed that the discharge at the spark-gap in the secondary circuit was unaffected by the capacity across the break in the primary circuit. In later experiments, when the current broken rarely exceeded 1 ampere, the capacity was removed.

The spark-gap was between platinum wires 2 mm. in diameter coated with glass to within 1 mm. of their ends, which were sharpened to fine points. These electrodes were sealed, with accurate alignment, into a glass globe of 75 c.c. capacity, so as to form a horizontal spark-gap, the globe being fitted at the top with a three-way tap (see T., 1917, **111**, 133, Fig. 2).

The mixtures of methane and air were prepared in glass gas-holders over a mixture of equal parts by volume of glycerol and water, and were analysed before use. The gas-holder containing the mixture to be experimented with was attached by means of stout rubber pressure tubing to one limb of the three-way tap on the explosion-vessel, a glass tube packed with cotton wool being interposed to serve as a filter. The other limb of the three-way tap made connexion, through a calcium chloride tower, with a vacuum pump.

The method of experiment was that of trial and error. A charge of a given mixture having been introduced into the explosion-vessel at atmospheric temperature and pressure, the current in the primary circuit was adjusted to an arbitrary value and the discharge caused to pass at the spark-gap. If ignition of the mixture occurred, the explosion-vessel was rapidly exhausted and a fresh charge allowed to enter from the gas-holder; this was allowed to remain for a few seconds, and then removed by exhaustion, the explosion-vessel being finally refilled.* The current in the primary circuit was now adjusted at a lower value; if the secondary discharge produced on breaking this current did not ignite the mixture during ten trials (made at intervals of about five seconds each), it was increased by 0·01 ampere, and ten further discharges were caused to pass. Eventually a value for the current in the primary circuit was found such that the secondary discharge,

* The object of this procedure was to avoid the condensation of moisture, produced by the combustion of the methane, within the explosion-vessel, and to maintain the same saturation of water-vapour in the mixtures throughout a series of experiments.

produced on breaking it at a constant rate, ignited the mixture within the first few trials, a current 0·01 ampere less in value giving, under the same conditions, a secondary discharge incapable of igniting the mixture in one hundred or more trials. The final value for the "igniting current" for a given mixture was checked by making four or five trials with fresh charges of the mixture at, and 0·01 ampere below, the current found in the preliminary trials.

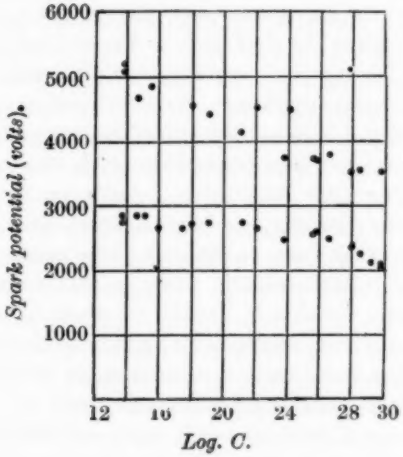
If a discharge was capable of igniting a mixture, it usually did so at the first, or within the first three, trials. That it did not do so invariably at the first trial is ascribable to slight alterations in the experimental conditions, either at the contact breaker or at the spark-gap. Ordinarily, the contrast between the current necessary to produce a discharge which would, and one which would not, ignite a given mixture was very sharp, the one, as aforesaid, causing ignition within the first two or three discharges, the other, 0·01 ampere less, being incapable under the same conditions of producing an igniting discharge, however often trial might be made. Occasionally, however, irregularities were observed, ignition of a given mixture perhaps occurring with the usual "igniting current" only after fifty discharges. Such an irregularity could always be traced to oxidation of the polished steel contacts of the primary circuit-breaker; on re-polishing the contacts, the irregularity disappeared. More rarely, when it was found that a much higher current than usual was unable to produce a discharge capable of igniting a given mixture, irregularity could be traced to the condition of the spark-gap; a minute speck of dust had perhaps lodged on one of the sparking-points. On such occasions, cleaning of the explosion-vessel with chromic and sulphuric acids restored the spark-gap to its original condition, a fact which was tested by trial of a "standard" mixture (8·5 per cent. of methane). As a matter of routine, the testing of this standard mixture was frequently interposed between dissimilar mixtures to give assurance that the conditions of experiment were being maintained unchanged.

I have described in some detail the precautions most necessary in carrying out work of this character, because the belief, first promulgated by Thornton (*Proc. Roy. Soc.*, 1914, [*A*], **91**, 17), that continuous alteration of the proportions of gas and air in an inflammable mixture can be accompanied by discontinuous alteration in the intensity of spark required for ignition, has recently been revived by Paterson and Campbell on their observance of an apparent discontinuity of a different kind (*loc. cit.*, p. 212).

Paterson and Campbell's observations were on the relation

between the capacity and the spark potential necessary to cause the ignition of a given gas mixture the composition of which remained the same throughout any one series of experiments. Two series of their observations are reproduced in Fig. 1, which is the authors' Fig. 9, without certain lines, intended to represent discontinuities or "steps," which they draw through the observed points. It will be seen that the results can be represented equally as well by a "smooth" as by a "stepped" curve. It does not appear from Paterson and Campbell's paper that these irregularities were invariably produced in the same positions on repeated trials (in which event they might properly be regarded as regularities, and some significance would attach to them), for the two

FIG. 1.

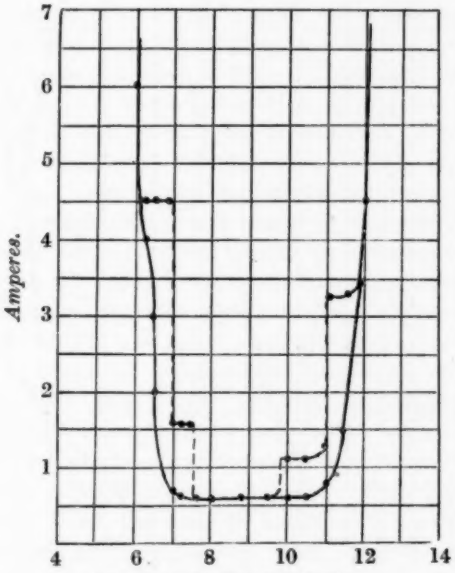


series of observations selected are stated to be unusually free from inconsistency. That being so, some unobserved lack of uniformity in the manner of carrying out the determinations would seem a reasonable explanation of the lack of uniformity of the results. At all events, it is rather far-fetched to relate, as do Paterson and Campbell, these inconsistencies in the physical characteristics of the discharge, supposing they exist, with the discontinuities in the chemical characteristics of inflammable mixtures presumed by Thornton.

Paterson and Campbell themselves obtained quite smooth curves relating the composition of different mixtures of hydrogen and air with the spark potential (of capacity sparks) required for ignition (compare Thornton, *loc. cit.*, p. 387). Their suggestion is that "the igniting-power of a spark is very much more sensitive to

changes in composition than to the capacity discharging in the spark; that is to say, a given percentage change in composition involves a very much greater percentage change of critical capacity. Accordingly, the effect of substituting as abscissa composition for capacity is much the same as diminishing very greatly the scale of abscissæ in Fig. 9, while the scale of ordinates is unchanged." This compression of the scale of abscissæ in Fig. 9 (Fig. 1 of this paper) would mask the irregularities. Hence arises "the failure of Wheeler and others to observe 'stepped ignition.' All those

FIG. 2.

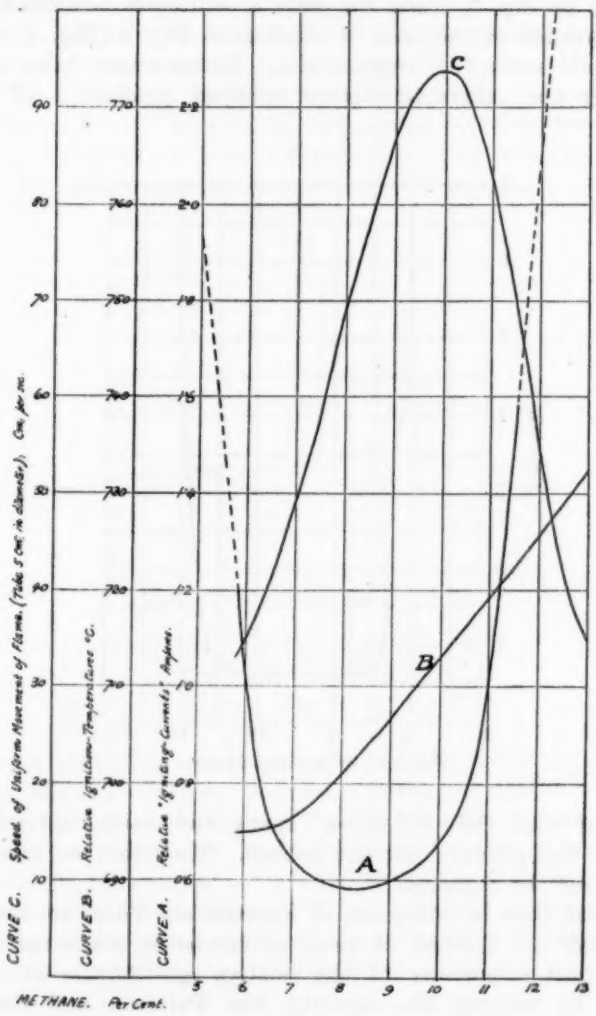


who failed used the 'induction' spark and varied intensity by means of the primary current broken. Thornton, on the other hand, varied the capacity."

It is true that in one series of experiments Thornton was concerned with the ignition of gases by condenser discharge sparks, and obtained a measure of the relative ignitibilities of certain mixtures by varying the capacity, but Paterson and Campbell ignore the fact that the most notable examples of discontinuity were recorded by Thornton when using "induction" sparks. The work of mine referred to in the sentence quoted above formed a direct check on experiments made in a similar manner by Thornton, and is so described (T., 1917, **111**, 130, 411).

The example of Thornton's stepped ignition which I was unable to confirm (ignition by the impulsive discharge of a mixture of methane and air, 9·5 per cent. of methane, the pressure of which was

FIG. 3.


C
B
A
CURVE C. Speed of Uniform Movement of Flame. (Tube 5 Cm. in diameter). Cm. per sec.
CURVE B. Relative Ignition-Temperatures °C.
CURVE A. Relative "Ignition-Currents" Ampères.
METHANE. Per Cent.

varied) was chosen as presenting few sources of error; for example, the composition of the mixture remaining unchanged, errror of analysis would not affect the results. Moreover, the steps recorded by Thornton were remarkably well defined. Thornton has, how-

ever, obtained a rather ill-defined stepped curve for the relation between the composition of mixtures of methane and air and their ease of ignition by the impulsive discharge, and, in view of Paterson and Campbell's suggestion, reference must be made to this work. The "stepped" curve is reproduced in Fig. 2. Thornton's comments thereon include the following (*loc. cit.*, p. 388): "With this kind of ignition methane appears to be sensitive to slight changes on the surface of the poles." "If the poles were not cleaned after every few explosions, steps occurred in the curve . . . which disappeared again when the poles were cleaned."

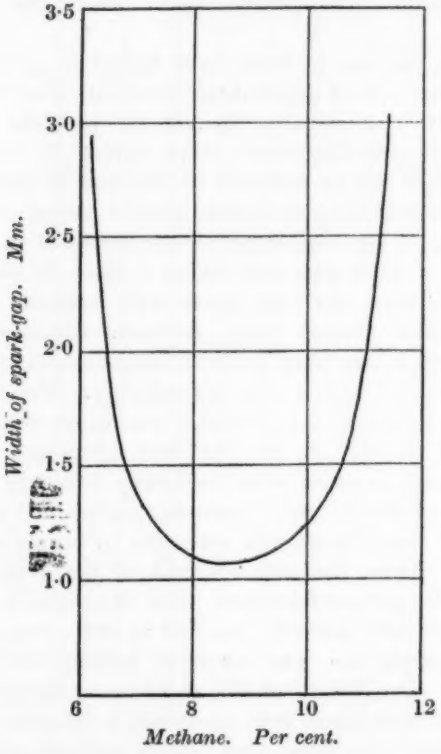
In other words, as was to have been expected, unless the conditions of experiment were maintained constant, discordant results were obtained. It is conceivable that all the peculiar discontinuities which have dogged Thornton's steps during his researches on the ignition of gases can be ascribed to the lack of similar precautions to that of maintaining the cleanliness of the electrodes.

Curve *A* in Fig. 3 represents the results obtained in the present research when the spark-gap was about 1 mm. in length. Four other curves have been obtained (each with between twenty and twenty-five observed points) using different explosion-vessels in which the spark-gap was also about 1 mm., and two curves for spark-gaps of about 0·5 and 3 mm. respectively. For the two last-named curves, the general experimental conditions were as for the curve reproduced in Fig. 3; for the four additional curves with a 1 mm. spark-gap, changes were purposely made in the experimental conditions (which were, however, maintained constant for any one series of experiments) in attempts to obtain some indication of "steps." Thus, the rate of break of the primary current, the voltage of the primary current, and the construction of the induction-coil were each altered; for two of the series (by different observers), the precaution was taken of leaving the observer in ignorance of the composition of the mixture undergoing test, lest a latent desire, if such there was, to obtain a smooth curve should unconsciously affect the care with which critical mixtures were tested. In no instance was any other than a smooth curve, comparable in every respect with that reproduced in Fig. 3, obtained.

If the current in the primary circuit of an induction-coil is maintained constant and the width of the gap in the secondary circuit is varied, a straight line relationship exists between the sparking voltage and the width of the gap, similar to that which exists, as already stated, between the primary current and the sparking voltage when the secondary gap (between sharply pointed

electrodes) is of constant width. A check on the validity of curve *A* of Fig. 3 can thus be obtained by plotting g^2 (secondary gap) or g against percentage of inflammable gas, i (primary current) being maintained constant. A series of determinations of this character was made, the electrodes being a disk of platinum 1 cm. in diameter and a sharply pointed cone of platinum attached to a micrometer head to admit of accurate measurement of the

FIG. 4.



width of the gap. The current in the primary circuit was maintained constant at 1·0 ampere. The curve obtained when width of gap in mm. was plotted against percentage of methane is reproduced in Fig. 4. It is identical in character with curve *A* of Fig. 3.

The characteristics of the curves (Fig. 3 [*A*] and Fig. 4) to which attention should be directed are: (1) the greatly increased difficulty of ignition as the limits of inflammability are approached, particularly on the high limit side; and (2) the position of a range

for optimum ease of ignition between 8·2 and 8·5 per cent. methane.

It should be noted that no attempt has been made to determine the limits of inflammability of the mixtures in the course of these experiments. Such determinations would only have been significant in relation to the explosion-vessel (of 75 c.c. capacity), the size of which did not admit of judging to what extent the continued propagation of flame was possible in the mixtures.

Moreover, mixtures which can be ignited by a sufficiently intense source of heat—and it is the problem of ignition with which we are now concerned—are not necessarily capable of propagating flame any considerable distance away from that source of heat. An illustration of this is to be found in the "cap" or aureole that warns miners of the presence of firedamp in coal-mines. An aureole due to burning methane can be seen around a non-luminous oil-flame when less than 1 per cent. of the gas is present in the air, and this aureole increases in size (mainly in length) as the percentage of gas is increased, until with 5 per cent. of methane it may be many inches long. The lower limit of inflammability of methane, however, even for upward propagation of flame, is not less than 5·3 per cent. Similarly, if a sufficiently intense electric spark is caused to pass in a mixture of methane and air containing but a trace of methane, a cap may be seen above the spark, and if the quantity of methane be 4 or 5 per cent., the momentary cap may be sufficiently large to fill the explosion-vessel. This production of large caps in small explosion-vessels has misled several observers into placing on record false limits of inflammability.

It will be understood, then, that mixtures which contain less inflammable gas than is required for a lower-limit mixture (or more than is required for an upper-limit mixture) can be ignited, and it may be important to determine the relative ignitibilities of such mixtures, as will be seen when the ignition of mixtures of air with the higher members of the paraffin series is considered.

The limits of inflammability, upward propagation of flame, for mixtures of methane and air are, lower, 5·3, and upper, 14·3, per cent., and a local inflammation can be obtained in mixtures beyond those limits. The determinations of "igniting-currents" were, in general, restricted to such mixtures as required no more than 1·25 amperes. For, apart from the fact that when currents higher than this were broken in the primary circuit, the need for re-polishing the surfaces of the contact-breaker became over-frequent, the form of the secondary discharge with a 1 mm. gap changed, inasmuch as it spread back along the electrode instead of appearing exclusively from the point, as it did when the current broken

in the primary circuit was not much more than 1 ampere, so that the size, as well as the intensity, of the source of ignition changed. Igniting currents higher than 1·25 amperes therefore did not bear a strict relation to those of lower value when a spark-gap of 1 mm. was used. With a spark-gap of 3 mm., no change in the form of the discharge appeared as the current in the primary circuit was increased up to 3 amperes, and the "igniting-currents" were, over the whole range of mixtures, lower with this gap than with the 1 mm. gap, so that the true relative ease of ignition of methane–air mixtures at the lower and upper limits of inflammability could, if necessary, be determined by the use of a wider spark-gap. The fact to be emphasised is that the terminal points on Curve *A* in Fig. 3 do not represent the "limits" of igniting-power of the discharges for the mixtures. Despite the steep slope of the curve towards those terminal points, the range of igniting-power of the discharge extends, as already explained, beyond the limits of inflammability of the mixtures, and the curve can be extended, as shown in dotted line. On the other hand, the graph reproduced in Fig. 4 is nearly complete. For with a constant current of 1·0 ampere in the primary circuit, mixtures containing less than 6·0 or more than 11·5 per cent. of methane could not be ignited by the secondary discharge under the conditions of the experiments, whatever the width of the gap. The reason for this will be explained in a subsequent communication.

Of the factors enumerated on p. 903 as determining, in general, the ignitibility of gaseous mixtures, the thermal conductivity and the specific heat of the mixture can be regarded as of relatively little importance so far as the range of mixtures of methane and air under examination is concerned. Similarly, the voltage of the spark can be regarded as unaffected by change in the insulating power of the mixtures, which is, indeed, practically constant. (In this connexion, see Wright, T., 1917, **111**, 643.) There remains to be considered the ignition-temperatures of the mixtures, the duration of the pre-flame period, and the initial speed of propagation of flame in them, and their thermal values.

When these factors are considered in conjunction with the characteristics of the igniting-source, which are "high intensity and exceedingly short duration," it will be realised that the relative ignition-temperatures, in themselves, of the mixtures are not likely to determine whether one mixture rather than another is more easily ignitible by such a source. For it can be assumed that the temperature to which the gases in the path of any of the discharges represented by the "igniting-currents" in Fig. 3 are raised is far in excess of the ignition-temperature of any of

the mixtures. The relative ignition-temperatures of mixtures of methane and air, when in contact with a heated surface, have been determined by Mason, whose work will be described in Part II of this research. A curve constructed from his determinations is reproduced in Fig. 3 (Curve *B*) for comparison with the "igniting-current" curve. The only relation between the two curves lies in the increasing difficulty in the ignition of mixtures rich in methane, or, to express the matter more significantly, poor in oxygen, disclosed by both. Any influence that the ignition-temperature of the mixtures may have on their ignition by the secondary discharge will therefore tend to cause the more ready ignition of mixtures containing an excess of oxygen.

A curve (Curve *C*) showing the relative speeds of propagation of flame ("uniform movement") in mixtures of methane and air over the same range is reproduced in Fig. 3 (see T., 1917, **111**, 1044). This curve is, with an important difference, which is referred to later, nearly the inverse of the "igniting-current" curve. The inference is that the intensity of the secondary discharge necessary to cause the ignition of a given mixture—necessary, that is to say, to ensure that flame shall travel away from the immediate vicinity of the discharge—is mainly dependent on the initial speed with which flame can travel in that mixture.

We know that there is combination of the gases in the path of a discharge which does not cause "ignition" of an inflammable mixture. Close observation of the discharges produced in the mixtures of methane and air by currents slightly less than the "igniting-currents" disclosed the fact that such discharges were accompanied by minute tongues of flame, which shot out above and below the spark-gap in the form of a V, with an inverted V above it $\left(\frac{\Lambda}{\mathrm{V}}\right)$. These tongues of flame were produced in all the mixtures of methane and air, but were more noticeable (because longer) in mixtures near the limits of inflammability, and most noticeable (because of the superior luminosity of the flame) near the upper limit. Moreover, with such mixtures the interval between the "igniting-current" and one which produced a discharge capable of forming these tongues of flame was greater than with the more readily ignitible mixtures.

The passage of the discharge, though it may cause the combination of the gases in its immediate vicinity, is incapable of resulting in the general ignition of a mixture unless the initial impetus it gives to the speed of propagation of flame in the mixture is sufficient to carry the flame through a sufficient volume. In amplification of this statement, I may quote from a report

prepared for the Explosions in Mines Committee of the Home Office (H.M. Stationery Office, Cd. 6704 of 1913): "Imagine a small sphere of hydrogen and oxygen 1 mm. in diameter at atmospheric pressure heated by an electric spark: the complete combustion of the gases in this sphere (the volume of which is about 0·5 cu. mm.) would yield less than the one-thousandth of a (small) calorie of heat. In order to spread the flame, this heat has to be communicated to the spherical shell of unburnt gas in contact with the sphere (the surface of which is 3·1 sq. mm.) and bring a certain thickness of that shell to its ignition-temperature. It may fail to do so. Let us suppose that the diameter of the heated sphere is doubled: the volume of gases fired is now eight times as large, whilst the surface is four times as large as before. By increasing the size (or the intensity) of the spark, a point is soon reached at which the combustion produced by the spark evolves enough heat to fire *per se* the adjacent gas-mixture—and the flame is propagated."

It will be understood, from these considerations, why the ease of ignition of an inflammable mixture by a momentary source of heat, such as the secondary discharge, is so dependent on the rapidity with which a sufficient volume of the mixture becomes ignited; that is to say, on the initial speed of propagation of flame in the mixture. This dependence, which will be shown in Part III of this research to obtain with inflammable gases other than methane, is not, however, complete. The mixtures of methane and air in which the initial speed of propagation of flame is fastest contain between 9·5 and 10·0 per cent. of methane, whilst the mixture most easily ignitible by the secondary discharge lies within the range 8·2 and 8·5 per cent. methane, the majority of the determinations inclining towards a percentage of 8·3.

The lower ignition-temperatures of mixtures of methane and air containing an excess of oxygen will, as already stated, cause them to be more readily ignited by an intense source of heat of short duration, and a simple explanation of the position of the range of mixtures most easily ignitible by the secondary discharge, an explanation which accounts also for the greatly increased difficulty there is in igniting by such means mixtures rich in methane, is that the curve for relative "igniting-currents" is compounded of the relative ignition-temperature curve and the inverse of the curve relating composition of the mixtures with initial speed of propagation of flame therein.

Experimental.

The determinations from which Curve *A* in Fig. 3 is constructed are as follow:

Methane. Per cent.	Relative "Igniting-current." Amperes.	Methane. Per cent.	Relative "Igniting-current" Amperes.
5·85	1·20	8·60	0·59
6·00	1·05	8·85	0·60
6·25	0·86	9·15	0·61
6·35	0·79	9·40	0·62
6·40	0·78	9·50	0·63
6·55	0·71	9·70	0·64
6·60	0·70	10·00	0·68
6·85	0·67	10·40	0·74
7·05	0·63	10·50	0·79
7·20	0·62	10·70	0·86
7·50	0·61	10·80	0·89
7·95	0·59	10·90	0·98
8·00	0·59	11·10	1·12
8·20	0·585	11·50	1·56

The curve in Fig. 4 is constructed from the following determinations:

Methane. Per cent.	Width of gap. Mm.	Methane. Per cent.	Width of gap. Mm.
6·20	2·94	8·90	1·09
6·50	1·95	9·45	1·13
6·95	1·39	9·90	1·23
7·40	1·22	10·50	1·42
8·05	1·10	11·05	1·98
8·30	1·08	11·35	2·75
8·50	1·08	11·40	3·02

For carrying out many of the laborious series of determinations rendered necessary by the fruitless search for "steps," I am indebted to my wife; for the numerous gas analyses required, Mr. T. Mason is responsible.

Home Office Experimental Station,
Eskmeals, Cumberland. [*Received, June 8th,* 1920.]

CIII.—*The Composition of Ancient Eastern Bronzes.*

By Masumi Chikashige.

Among the various examples of ancient Japanese and Chinese art, the bronzes are most suitable for the purpose of examining the nature of ancient metallurgical methods. They resist the corrosive action of time much better than do other common alloys or metals

and preserve the features of ancient art correctly. Brass articles are not so antique as bronze. They date from about the tenth century, that is, the beginning of the Sung dynasty.

As excavated objects are always covered with rust, it has been the custom to remove this before analysis. Since, however, the constituents of an alloy, which is simply a mixture, would retain their individual properties, the rate of rusting must differ in the case of each metal. In bronze, a selective corrosion takes place in the order: lead, copper, and tin. The metallic proportions in the rust will differ from those in the original alloy, becoming much enriched with copper. Montelius, in his "Chronologie der ältesten Bronzezeit," 1900, p. 151, gives the following analysis of two similar Egyptian rings:

	I.	II.
Copper.....	79·51	16·23
Tin	9·65	75·66

The first ring seems not to have undergone much change, but the second must have lost most of its copper by oxidation. It is obvious, therefore, that it is not correct to remove the rust and to submit what remains only to analysis.

The author's method of analysis is therefore to remove earthy matter from a rusted article and to analyse rust and metal together. This gives, of course, too low a percentage for the metallic constituents, which should therefore be recalculated for 100.

Even this method becomes objectionable in a case where the composition of the rust has undergone change by a partial solution or disintegration before analysis. This is due, not to an incorrect method, but to lack of the right samples.

Mirrors.

The ancient bronze mirrors may be divided into four classes, namely, white, pale yellow, deep yellow, and red, according to their surface colours. These differences in colour are due to the amounts of tin becoming less and less, and corresponding exactly with the chronological period in which the mirrors were made. In the most recent times, zinc is employed instead of tin, giving rise to the use of brass mirrors. The mirrors belonging to the white and pale yellow class were effective without further alloy, but those belonging to the other classes, together with the brass, had necessarily to be alloyed with mercury before use. Brass as well as bronze objects with less tin are, however, more easily cast, and they were rapidly adopted, probably with the invention of amalgamation, in the East.

The following is a summary of analyses of bronze mirrors differing in ages and compositions:

FIG. 1.

FIG. 2.

FIG. 3.

FIG. 4.

(*To face p.* 918, *Trans.*

FIG. 5.

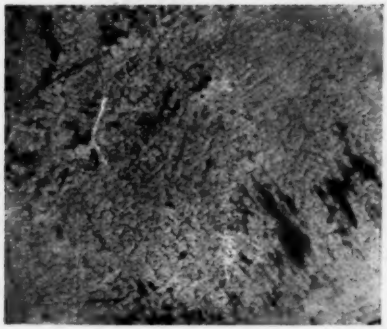


FIG. 6.

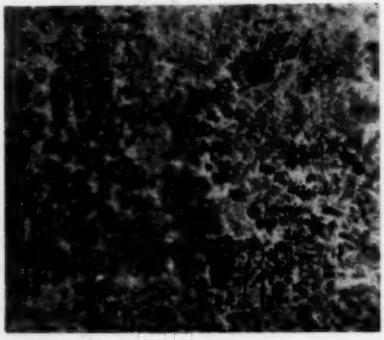


FIG. 7.

FIG. 8.

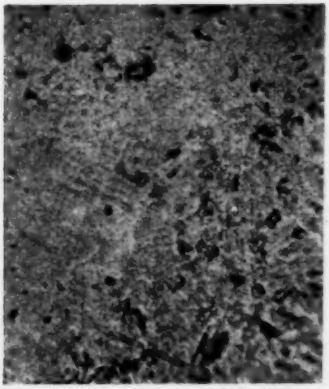


FIG. 9.

No.	Sample.	Class.	Age and place of excavation.	Form.	Copper	Tin.	Lead.	Zinc.	Iron.	Arsenic.	Anti-mony.	Nickel.	Silver.	Gold.	Copper

No.	Sample.	Class.	Age and place of excavation.	Form.	Copper	Tin.	Lead.	Zinc.	Iron.	Arsenic	Anti-mony.	Nickel.	Silver.	Gold.	Copper to tin.
1	Chinese bronze mirror.	White	I. Cent. (Hau-Dyn.): excav. in China.	Fig. 1	65·10	25·07	9·12	0·16	0·06	trace	trace	—	—	—	72 : 28
2	„	„	„		66·67	26·57	5·29	0·20	0·81	—	—	0·63	—	—	72 : 28
3	„	„	„		62·15	26·47	5·29	5·00	—	—	1·08	—	trace	—	70 : 30
4	„	„	„		70·11	24·28	5·59	—	0·22	—	—	—	„	—	74 : 26
5	„	„	VII. Cent. (T'au-Dyn.): excav. in China.		67·56	27·57	5·43	—	0·37	—	—	—	„	—	71 : 29
6	„	„	I. Cent. (Hau-Dyn.): excav. in Japan.		62·99	24·12	3·97	—	—	2·63	—	1·83	—	—	72 : 28
7	„	„	„		67·22	25·44	0·61	6·73	—	—	—	—	—	—	72 : 28
8	„	„	„		65·82	28·72	5·05	—	—	—	—	—	—	—	70 : 30
9	„	„	„		68·63	30·69	0·69	—	—	—	—	—	—	—	69 : 31
10	*Japanese bronze mirror.	Pale yellow	V. Cent. (made in Japan) : excav. in Japan.		67·03	22·45	8·99	—	—	—	—	1·52	—	—	75 : 25
11	Corean bronze mirror.	„	Not certain	Fig. 2	65·37	21·90	9·68	—	—	0·44	2·60	—	—	—	75 : 25
12	Corean bronze mirror.	Deep yellow	X. Cent. : excav. in Corea.	Fig. 2	72·99	11·76	15·14	—	0·29	—	—	—	0·09	0·23	—
13	Japanese bronze mirror.	„	XI. Cent. : preserved in Japan	Fig. 3	74·04	9·29	5·67	—	0·89	1·68	1·55	0·88	—	—	—
14	Chinese bronze mirror.	„	XII. Cent. (Kin-Dyn.): found in China.	Fig. 4	65·11	11·58	20·49	—	—	0·13	2·35	0·34	—	—	—
15	Chinese brass mirror.		XIX. Cent. (Ch'in - Dyn.): preserved in China.	Fig. 5	74·00	3·29	7·59	12·96	—	trace	1·81	0·35	—	—	—
16	„		„		58·52	5·58	7·66	23·29	1·78	—	—	3·17	—	—	—

* Recipe of a Japanese mirror at Yengishiki : 76 per cent. of copper to 24 per cent of tin.

As may be seen from the table, the white bronze was made from the first century, and probably from much earlier times, down to the seventh century. It contains, on the average, 67 per cent. of copper, 27 per cent. of tin, and 6 per cent. of lead as its principal constituents, the average ratio of copper to tin being 71:29; the alloy corresponds, therefore, with the ϵ-phase in the copper–tin diagram, which is a solid solution of tin in copper, and known as specular metal. The presence of lead is not to be regarded as useless; it reacts with neither copper nor tin, but lies between the granules of the solid solution, acting as a cement. The author was able to make a very good bronze mirror with these constituents. Without lead, the product is too brittle to be polished. Too slow cooling must, naturally, be avoided, in order to prevent separation of the lead. The ancients were clever enough to take advantage of the great hardness of the white bronze; the figures on the back of such mirrors usually consist of very fine, but deeply cut, lines, which have resisted wear for two or three thousand years.

However bright the white bronze mirror may be, its reflective power is not so great as that of a silver mirror, absorption of the light taking place very much in the blue. A determination with the author's imitation metallic mirror gave the following figures: blue 40 per cent., yellow 50 per cent., and red 60 per cent. The objects reflected therefore seem much redder than they are in reality.

Weapons.

As weapons must be both hard and tough, the white bronze cannot be used for their manufacture, and that the bronze with 10—20 per cent. of tin suits best seems a fact well known to the ancients. They knew, too, that in order to make the casting easier, some antimony could be added without any of the hardness being lost.

Two samples of arrow-heads of the Han dynasty were analysed, with the following results:

	I.	II.
Copper	74·47	73·12
Tin	10·82	16·15
Antimony	8·00	8·69
Nickel	3·68	2·04
Iron	3·03	trace
Arsenic	trace	trace

Since antimony dissolves in copper as well as in tin, the above samples might be thought to be similar to one composed of 85 per cent. of copper and 15 per cent. of tin, ignoring the other small admixtures, but the alloys with the above compositions have

quite different structures, as is seen from those of the arrow-heads shown in Figs. 6 and 7. An ingot with the same composition as the arrow-head, No. 1, was prepared and quenched at 680° after half an hour's heating. Its structure was changed from the ordinary polygonal (Fig. 8) to the fine acicular (Fig. 9), which is quite similar to that of the arrow-head. The hardness of the bronze with 10 per cent. of tin is only 12 on Shore's scale, whilst that of the arrow-head, No. 1, is 15—17. The author's imitation sample was also 10—12 before quenching, but after quenching it had risen to 15. The ancients had probably no intention of quenching; they arrived at such a result unexpectedly by way of moulding.

A Japanese arrow-head excavated in the Province of Tango has the composition (I), and must certainly have been less sharp than

	I.	II.
Copper	96·48	90·28
Tin	2·46	3·20
Lead	0·56	0·28
Arsenic	0·50	0·03
Iron	—	5·60

those described above. The age is not certain, but a bronze coin, "Wadô Kaihô," made in the seventh century, has almost the same composition (II). They might perhaps have some relation to each other.

Swords and halberds excavated in Japan and China were analysed, with the following results:

Samples.	Copper.	Tin.	Antimony.	Arsenic.	Nickel.	Iron.	Lead.	Copper : Tin.
Sword: Shantung, China.	73·34	19·84	3·80	0·55	2·47	—	—	78 : 22
Sword: Shantung, China.	69·31	12·55	2·30	3·01	3·52	1·37	7·92	84 : 16
Halberd: Shantung, China.	73·35	17·48	—	trace	—	—	9·17	80 : 20
Sword: Prov. of Chikuzen, Japan.	76·60	14·13	4·93	trace	2·93	0·09	1·32	84 : 16

The proportions of copper to tin are correct, but the large amount of lead in some of them cannot be commended.

Musical Instruments.

Bell metal with a high percentage of tin is sonorous, but too brittle. The ancients were in the habit of using an alloy with rather less tin. An excavated Japanese bell, which dates from before the eighth century A.D., has the composition (I):

	I.	II.
Copper	68·96	82·90
Tin	15·45	9·93
Lead	5·63	—
Antimony	8·32	2·60
Iron	0·04	1·38
Nickel	1·35	0·79
Arsenic	trace.	1·68
Gold	—	0·71

Statues.

A small gilded Buddhist statue of the Six Dynasties (third century) has the composition (II).

Money.

The ancient Chinese coins generally contain less tin with much lead, so that some of them can scarcely be called bronze. The following are the results of analyses made with a few kinds of Chinese money current at the time of the "Spring and Autumn Annals," 722—481 B.C.:

Coin.	Copper.	Tin.	Lead.	Antimony.	Iron.	Arsenic.	Nickel.	Silver.
Bell money...	67·53	16·52	10·84	1·83	—	2·36	0·92	—
Knife money	46·22	9·25	43·53	—	0·73	—	—	0·27
" "	38·38	1·66	55·41	—	2·66	0·60	1·03	—
" "	45·93	2·12	48·60	—	—	1·72	1·63	—
" "	42·25	2·12	47·32	—	—	3·28	5·08	—
" "	64·65	6·76	21·25	—	0·41	3·88	3·04	—
Spade money	70·42	9·92	19·30	—	—	—	0·35	—

Spoons, etc.

Corean bronze, called "Sahari," or sometimes "Sonorous copper," usually occurs in the form of spoons, water-pots, etc. Very old spoons are usually covered with a velvet-black rust, but seldom with green carbonates. They give, on analysis, the following numbers:

	Copper.	Tin.	Nickel.	Zinc.	Arsenic.	Iron.	Lead.
Ancient spoon	73·77	24·04	2·19	—	—	—	—
New "	77·19	21·62	—	0·20	—	—	—
Ancient water pot	77·89	19·35	—	—	3·82	0·09	0·77

The alloy is therefore similar to the pale yellow bronze mirror. It sometimes exhibits a very beautiful structure consisting of large crystals, α and ϵ. The alloy is strongly resistant against rusting and is well suited for the purpose to which it is put by the Coreans.

The author is much indebted to his friends Mr. Fukuda, Mr. Matsuno, and Mr. Harada for their kind help in most of the analyses given in this paper.

KYOTO, JAPAN. [*Received, February 20th*, 1920.]

Helium: its Production and Uses.

A Lecture Delivered before the Chemical Society on June 17th, 1920.

By John Cunningham McLennan.

In 1868 Janssen (*Compt. rend.*, 1868, **67**, 838) drew attention to the existence of certain lines hitherto unobserved in the solar spectrum, which we now know are given by the element helium. In the same year, Frankland and Lockyer (*Proc. Roy. Soc.*, 1868, **17**, 91), from their observations on these spectral lines, were led to announce the existence of an element in the sun which up to that time had not been found on the earth. To this element they gave the name helium.

In 1882 the discovery was made by Palmieri (*Gazzetta*, 1882, **12**, 556) that the helium spectrum could be obtained from rocks and lavas taken from Vesuvius.

In the United States of America, Hillebrand in 1890 (*Bull. U.S. Geol. Survey*, 1890, No. 78, p. 43) succeeded in obtaining a quantity of gas from the mineral uraninite, which from chemical and spectroscopic tests he concluded was nitrogen. This gas we now know was, in fact, helium.

Finally, in 1895, Sir William Ramsay (*Chem. News*, 1895, **71**, 151) discovered that a gas could be obtained from the mineral cleveite. This gas he purified, and, on examining its spectrum, he found it to be the long-sought-for element helium. From 1895 up to the present, investigation has shown that helium is widely diffused throughout the earth. It can be obtained from many types of rocks, minerals, and earths, and it is present in varying amounts in practically all natural gases and spring waters. It is present too in the atmosphere of the earth to the extent of about four parts in one million by volume.

The gases from some springs in France have been shown to contain as much as 5 per cent. of helium. In the Western States of America, especially in Texas, natural gases exist which contain from 1 to 2 per cent. of helium, but within the British Empire no natural gases which have been examined show a helium content as high as 0·5 per cent.

Until the spring of 1918, not more than 3 or 4 cubic metres of helium had, in the aggregate, been collected, and its market price, though variable, was about £300 per cubic foot.

The principal characteristics of helium are:

(1) Its extreme lightness. It is only twice as heavy as hydrogen, the lightest element as yet isolated.

(2) Its absolute inertness. All attempts to effect combinations of helium and the rare gases, neon, argon, krypton, and xenon, as well, with other elements have as yet failed.

(3) Its close approximation to an ideal or perfect gas. It is monatomic, and is liquefiable at a temperature below that of liquid hydrogen. By causing liquid helium to evaporate in a vacuum, Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 493) has succeeded in reaching a temperature within 1° or 2° of the absolute zero.

(4) Its low sparking potential. Electric discharges can be passed through helium more easily than through most other gases.

No element has had a more romantic history than helium, and none is of greater interest to men of science than is this gas at the present time. Its formation as a disintegration product of the radioactive elements, and the identity of the nuclei of helium atoms with α-rays, give it a unique position among the elements.

Intense interest has been aroused by Sir Ernest Rutherford's recent discovery that in the nuclei of helium atoms in the form of α-rays we have a powerful and effective agent for disintegrating and simplifying the nuclei of atoms generally. This discovery points the way to still further progress. In the past, helium has been considered a rare and precious gas. To-day it is being produced in large quantities, and in view of the proposal now being put forward to use this gas in place of hydrogen as a filling for airships, one is apt to consider it to be not so precious as heretofore. It may be, however, that such vast and vitally important directions will suddenly be opened up in which helium can be utilised that the conservation of the gas, while it is still available to us, will become a matter of the first importance.

Shortly after the commencement of the war in 1914, it became evident that if helium were available in sufficient quantities to replace hydrogen in naval and military airships, losses in life and equipment would be very greatly lessened.

The fact that helium is both non-inflammable, non-explosive, and possesses 92 per cent. of the lifting power of hydrogen, makes it a most suitable filling for airship envelopes. By the use of helium, the engines of airships can be placed within the envelope if desired. A further advantage possessed by helium over hydrogen is that the buoyancy may be increased or decreased at will by heating and cooling the gas by electric or other means, which fact may possibly lead to considerable modifications in the technique of airship manœuvring and navigation. Moreover, the loss of gas from diffusion through the envelope is less with helium than with hydrogen to the extent of about 30 per cent.

Although there are indications that proposals had been put forward during the war by men of science in allied and enemy countries, as well as in the British Empire, regarding the development of supplies of helium for aeronautical purposes, it should be stated that the movement that led up to the investigation which it was my privilege to undertake was initiated by Sir Richard Threlfall. The existence in America of supplies of natural gas containing helium in varying amounts was known to him and others, and preliminary calculations as to the cost of production, transportation, etc., which he made led him to believe that there was substantial ground for thinking that helium could be obtained in large quantities at a cost which would not be prohibitive.

His proposals were laid before the Board of Invention and Research of the British Admiralty, and in the autumn of 1915 the author was asked by that Board to determine the helium content of the supplies of natural gas in Canada, and later on of those within the Empire, to carry out a series of experiments on a semi-commercial scale with the helium supplies which were available, and also to work out all technical details in connexion with the production of helium in quantity, as well as those relating to the re-purification, on a large scale, of such supplies as might be delivered and become contaminated with air in service. The present paper aims at giving a brief account of this investigation.

Composition of the Natural Gases Investigated.

In commencing the investigation, a survey was made of all the natural gases available in larger or smaller quantities within the Empire with a view to ascertain their helium content. Natural gases from Ontario and Alberta, Canada, were found to be the richest in helium, and these sources, it was found, could supply from 10,000,000 to 12,000,000 cubic feet of helium per year. The following is a summary of the results obtained from the analyses of a number of the gases investigated. They include, it will be seen, a few samples from outside the Empire. For a complete account of this part of the investigation, the reader is referred to Bulletin No. 31 of the Mines Branch, Department of Mines, Canada, 1920.

(a) *Ontario Gases.*—The analysis made by Profs. Ellis, Bain, and Ardagh (*Report of Bureau of Mines of Ontario*, 1914) of the natural gases supplied to the experimental station, initially set up at Hamilton, Ontario (Blackheath System), is as follows:

Methane	80 per cent.
Ethane	12 „
Nitrogen	8 „

It was found, however, on operating with this gas that the percentage assigned to methane really included a considerable proportion of gasoline, pentane, and butane as well. The helium content of the gas was found to be 0·34 per cent.

(b) *Alberta Gases.*—Gas taken from the mains leading from the Bow Island supply to Calgary was found to be quite free from the heavier hydrocarbons. At times it contained slight amounts of water vapour and occasionally a trace of carbon dioxide as well. Its approximate composition is given under I.

	I.	II.
Helium	0·33 per cent.	0·36 per cent.
Methane	87·6 ,,	91·6 ,,
Ethane	0·9 ,,	1·9 ,,
Nitrogen	11·2 ,,	6·14 ,,
Carbon dioxide	trace	trace
Water vapour	trace	trace

One well in particular, namely, No. 25 Barnwell, which has recently been driven, and now supplies gas to the system, was found to have a product of the composition II.

(c) *New Brunswick Gases.*—Some natural gases obtained from wells struck near Moncton, New Brunswick, Canada, were examined, and found to have the following composition:

Methane	80·0 per cent.
Ethane	7·2 ,,
Carbon dioxide	None
Oxygen	None
Nitrogen	12·8 per cent.
Helium	0·064 ,,

(d) *New Zealand Gases.*—A series of samples of the natural gases from the Hanmer, Kotuka, Weber, Blairlogie, and Rotorua supplies in New Zealand were forwarded by Mr. J. S. McLaurin, Dominion Analyst of Wellington, New Zealand, for examination, but were found to have an insignificant helium content, the richest containing not more than 0·077 per cent.

(e) *Italian Gases. Pisa.*—A sample of the natural gas brought by pipe to the city of Pisa, in Italy, was examined, and found to have the following composition:

Methane	80·0 per cent.
Ethane	4·0 ,,
Carbon dioxide	3·5 ,,
Nitrogen	11·9 ,,
Oxygen	0·6 ,,
Helium	None

(f) *Miscellaneous Analyses.*—An analysis of the natural gas supply from Heathfield, Sussex, England, showed it to have a helium content of but 0·21 per cent. The gas from the King

Spring, Bath, England, was found to contain 0·16 per cent. of helium, and analyses of natural gases obtained from Trinidad and from Peru showed their helium content to be negligible. An interesting observation was made in connexion with natural gases obtained from Pitt Meadows, Fraser River Valley, and Pender Island, in the Gulf of Georgia, British Columbia. Both these gases were found to have a nitrogen content of more than 99 per cent.

Preliminary Experiments.

Soon after taking up the investigation, it was found, as mentioned above, that large supplies of helium were available in the natural gas fields of Southern Alberta, and that a small supply could be obtained from a gas field situated about twenty-five miles to the south-west of the city of Hamilton, in Ontario. In 1917 the Board of Invention and Research decided to endeavour to exploit these sources of supply, and operations were begun by setting up, as already stated, a small experimental station near the city of Hamilton.

At this station, efforts were directed towards constructing a machine which would efficiently and economically separate out the helium frcm the other constituents present in the natural gas. The carrying out of this work expeditiously was made possible through the hearty co-operation of L'Air Liquide Société of Paris and Toronto, who generously lent, free of cost, a Claude oxygen column and the necessary auxiliary liquefying equipment for the investigation.

By making suitable additions to, and modifications in, this oxygen rectifying column, it was ascertained that the problem of separating, on a commercial scale, the helium which was present in this crude gas to the extent of only 0·33 per cent. was one capable of satisfactory solution. Early in 1918 it was found possible to raise the percentage of helium in the gas to 5·0 by passing it through the special rectifying column once only, and as the gas obtained in this way consisted of nitrogen and helium with a small percentage of methane, it became therefore a comparatively simple matter to obtain helium of a high degree of purity. In one particular set of experiments on this final rectification, helium of 87 per cent. purity was obtained.

Experimental Station at Calgary, Alberta.

In order to operate on the natural gas of the Bow Island system in Southern Alberta, an experimental station was established at Calgary in the autumn of 1918, and, starting with the knowledge

acquired through the preliminary operations at Hamilton, rapid progress was made in developing a rectification and purifying column, together with the requisite auxiliary equipment, which would efficiently and cheaply separate the helium from the natural gas.

The experimental station at Calgary consisted of a brick building of moderate dimensions, a small brick hut, and a galvanised iron balloon shed, located on the property of the Canadian Western Natural Gas, Light, Heat, and Power Company. The equipment in these buildings included that necessary to furnish an adequate supply of gas, which consisted of the requisite piping, gate valves, pressure-reducing valves, etc., a gasometer and two balloons, a number of gas cylinders, and the rectifying column with its expansion engine, together with the necessary compressors and a complete gas-testing outfit.

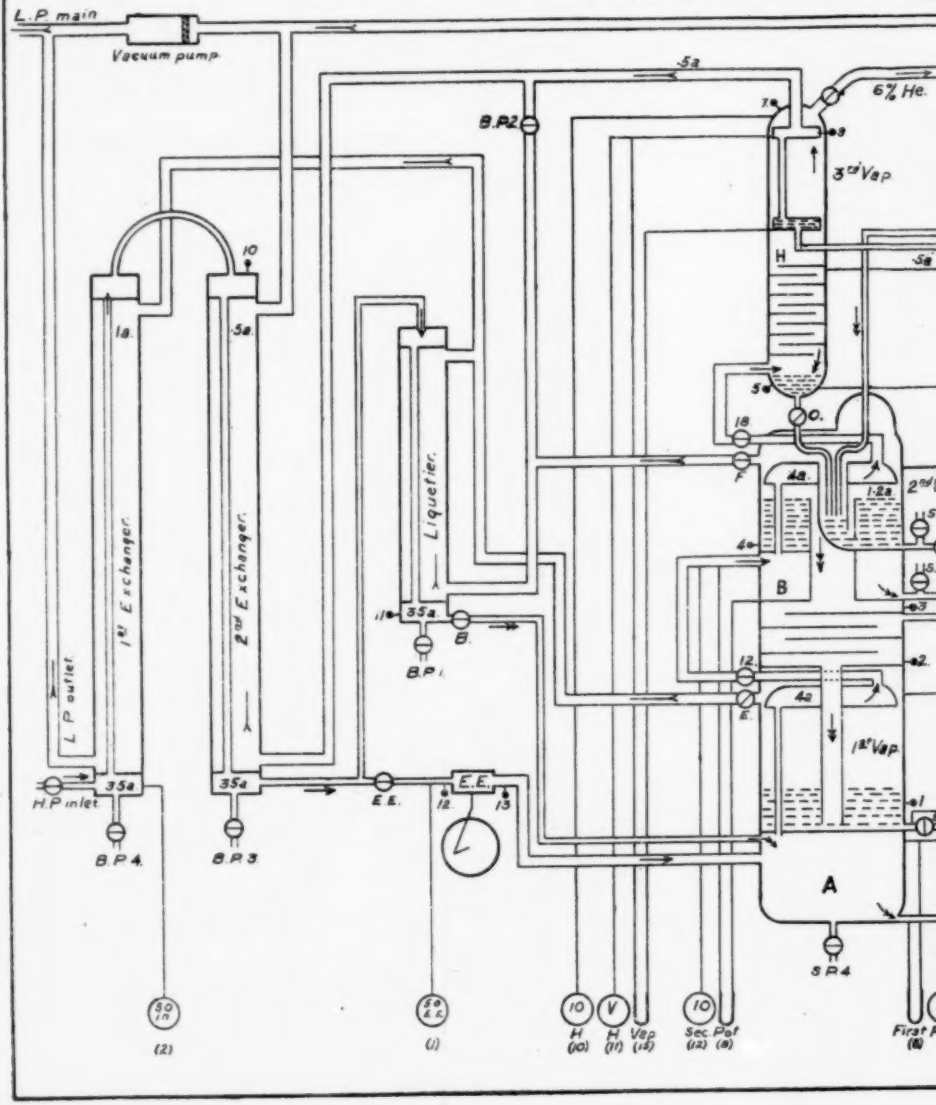
Development of the Rectification Column.

In proceeding to develop an equipment for separating the helium from the other constituents of natural gas, three lines of attack appeared to be open, namely, (*a*) by producing the refrigeration necessary to liquefy all the gases except the helium by the cold obtainable from the natural gas itself, (*b*) by using external refrigeration entirely, such as that obtainable with ammonia, carbon dioxide, liquid air, liquid nitrogen, etc., and (*c*) by combining methods (*a*) and (*b*).

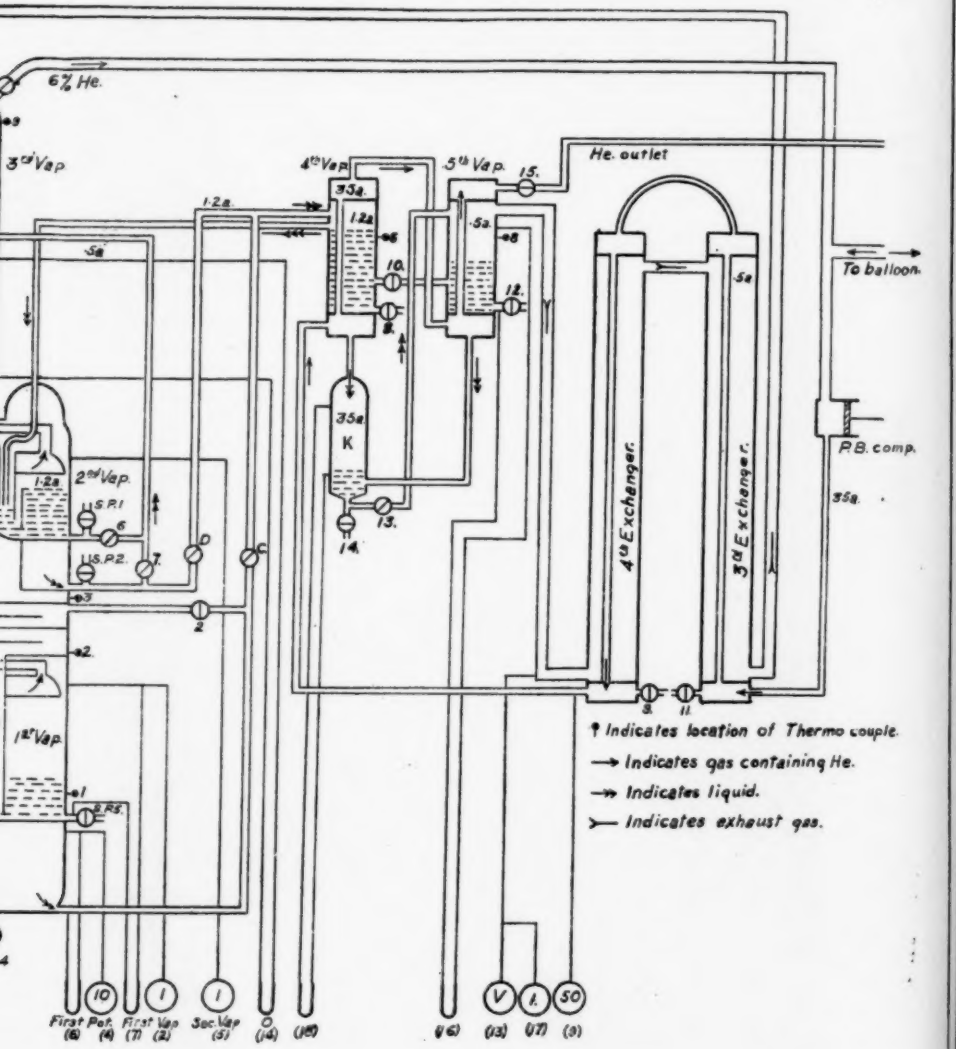
The last method had been successfully used for the production of helium by the naval authorities of the United States in the Texas field, but from the information supplied it did not appear that this process could be considered to be an economical one.

The preliminary experiments at Hamilton, Ontario, made it abundantly clear that method (*a*) was very promising and likely to be both efficient and economical. It was therefore adopted. It was evident from the start that to produce an efficient method the main difficulty to overcome would be the securing of a proper balance between the heat exchangers, the liquefier, the vaporisers, and the rectification portions of the machine. A machine was therefore designed, constructed, and supplied with piping which possessed great flexibility, and, in its general scheme, followed the lines of the Claude oxygen-producing column. It is unnecessary to go into details regarding the operation of this machine. It will suffice to say that it was tested under a variety of conditions. Notes were taken of the temperatures reached at different points in the machine under equilibrium conditions when the gas was passed through it in various ways. As a result of this procedure,

EXPERIMENTAL HE



AL HELIUM COLUMN



it was soon found what parts of the machine could be eliminated and what parts could be modified with advantage. When those changes were made which seemed desirable in the light of the experience gained, it was found that a machine had been evolved which would give highly satisfactory results.

A sketch of the experimental machine as it was finally constructed is shown in Plate I. With this machine, the process of separating the helium consisted of two operations. In the first, the compressed gas was passed through the heat exchangers, thence through the liquefier and the expansion engine to the bottom of the column at *A*. The uncondensed gas passed up through the first vaporiser, then through the valve, No. 12, to *B*. What was still uncondensed passed out through valve No. 18 to the bottom of the rectification column *H* and up over the third vaporiser, where more of the gas was condensed, and the final product, containing from 5 to 6 per cent. of helium, was drawn off. The liquid from *A* was passed through the valve *C* to the fourth vaporiser, from which it would overflow into the second vaporiser. The condensed liquid from *B* could be passed through *D* to the fourth vaporiser or through valve No. 7 to the third vaporiser. Some of the cooling liquid in the second vaporiser could also be passed through valve No. 6 to the third vaporiser when desired. In the second operation, the first product, containing 5 per cent. of helium, the remainder being principally nitrogen with a small percentage of methane, was compressed by a small compression pump to from 20 to 30 atmospheres, and passed through the third and fourth heat exchangers to the fourth vaporiser. Here some of it was condensed by the liquid methane produced in the first operation, and this condensed liquid flowed into the collecting bottle, *K*. The uncondensed gas still at 20 to 30 atmospheres passed, as shown in the sketch, into the fifth vaporiser, where almost all the nitrogen was condensed, and the final product was drawn through valve No. 15. The fifth vaporiser, it will be seen, was supplied with the liquid drawn from the bottle, *K*. It could also be supplied, if desired, by liquid from the fourth vaporiser through the valve No. 10. The level of the bottle was so arranged that there would be about 3 or 4 inches of liquid at the bottom before it showed on the gauge. By keeping the liquid just showing in the gauge, it was possible to prevent the gas from being drawn off with the liquid. In order to keep the temperature in the fifth vaporiser as low as possible, the gas from the evaporating liquid in it was drawn off through the third and fourth heat exchangers by means of a powerful vacuum pump.

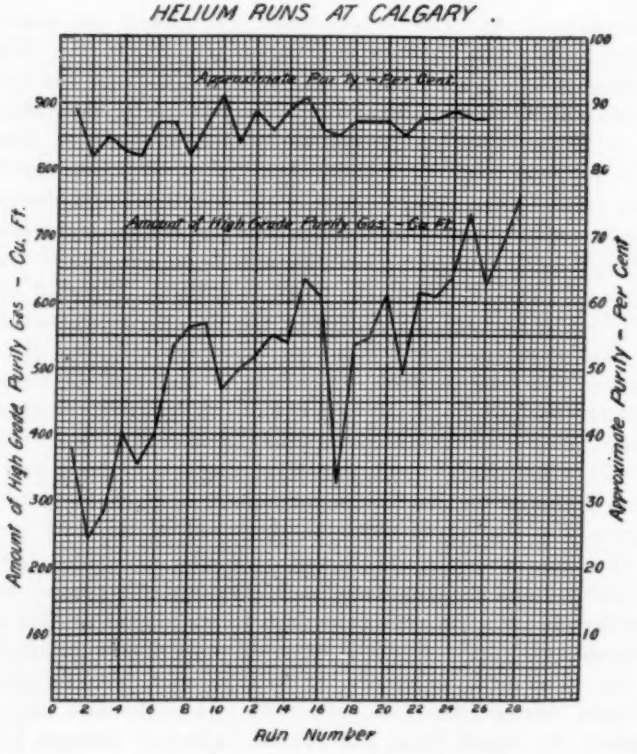
In operating with this machine, it was found that helium of

87 to 90 per cent. purity could be regularly and continuously produced.

Operations.

The experimental machine just described was used continuously for a series of trial runs from December 1st, 1919, to April 17th, 1920. The object of carrying out these trials was to gain as much knowledge as possible of the best running conditions. In the

FIG. 1.


HELIUM RUNS AT CALGARY.
Approximate Purity - Per Cent.
Amount of High Grade Purity Gas - Cu. Ft.
Amount of High Grade Purity Gas - Cu. Ft.
Approximate Purity - Per Cent
Run Number
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
100 200 300 400 500 600 700 800 900
10 20 30 40 50 60 70 80 90 100

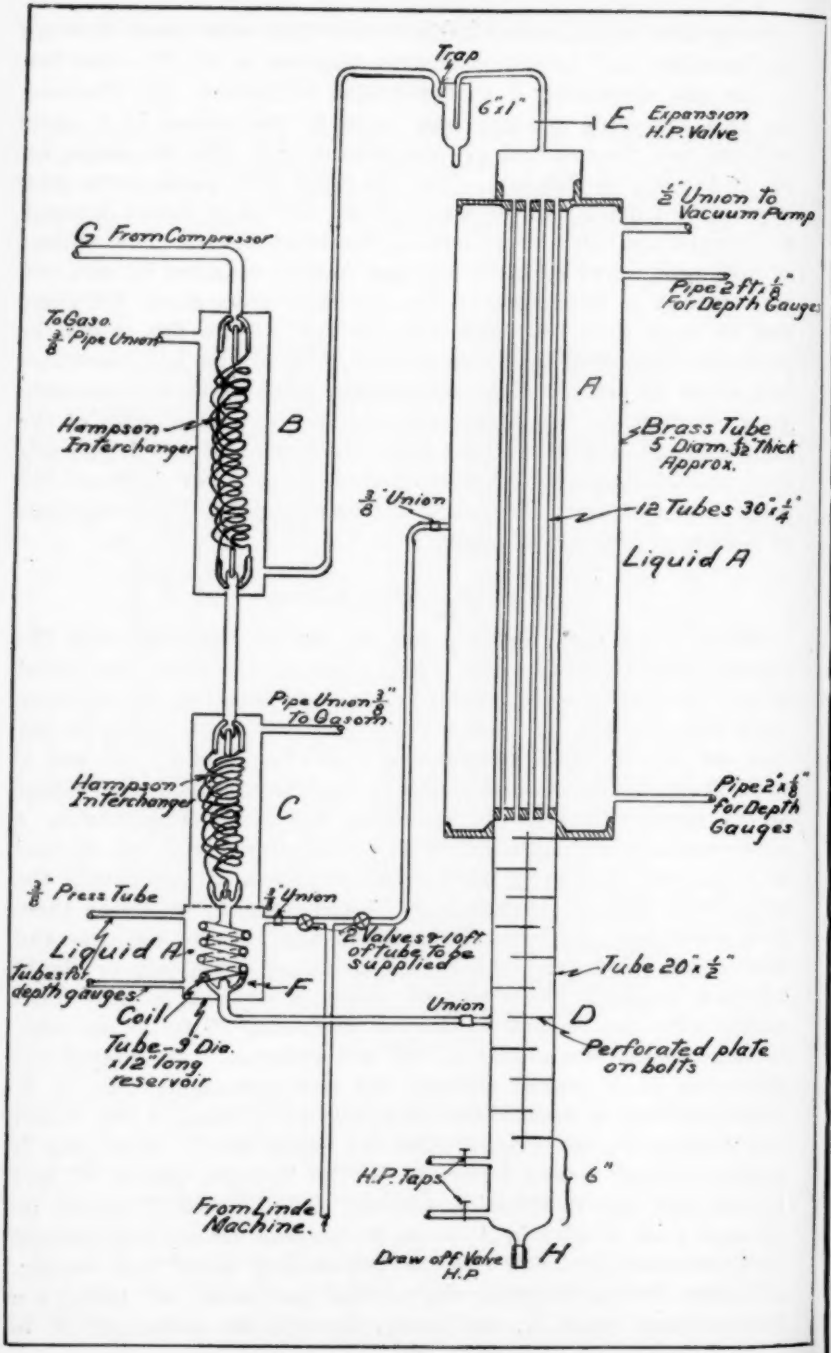
course of the four months' operations, numerous small modifications were made in the apparatus. Losses due to leaks were stopped and valve regulation was greatly improved. As a result of the operations, a steady increase was made in the output of helium of high purity.

The trials were made in successive runs, as it was necessary to shut down at intervals to refill the desiccators with sodium hydroxide.

In making a run, about 500,000 cubic feet were passed through the machine, and from this amount upwards of 20,000 cubic feet of the gas, containing 5 to 6 per cent. of helium, was obtained. As this low-grade product was made it was stored in a large balloon, and the residual gas was passed back into the mains for use in the city of Calgary. The 5 to 6 per cent. product was compressed to from 20 to 30 atmospheres, and then passed through the fourth and fifth vaporisers, as described above. The amount of final product, of 87 to 90 per cent. purity, obtained in each run rose steadily in the course of the operations from about 300 cubic feet to more than 700 cubic feet per run. From this it will be seen that the efficiency obtained with each of the two operations was about 67 per cent. In special runs made under exceptionally good conditions, a still higher efficiency was obtained. One of the curves given in Fig. 1 shows that the purity of the high-grade final product was steadily maintained in the series of runs, and the other curve exhibits the steady increase made in the production of helium of high-grade purity.

High-grade Purification.

When it was seen that the highest purity obtainable with the experimental machine under actual running conditions was about 90 per cent., steps were taken to design and construct an auxiliary piece of apparatus for raising the purity of the gas up to 99 per cent. or higher. This apparatus is shown in Plate II. *A* and *F* were two receptacles which could be kept partly filled with liquid air or liquid nitrogen. In operating this piece of apparatus, a high vacuum was maintained in *A*, but the liquid in *F* was allowed to evaporate at atmospheric pressure. It was arranged that the gases from both receptacles could be conserved by collecting them in a gasometer, and so rendering them available for use over and over again in closed cycle by the auxiliary liquid air or liquid nitrogen machine. In order to obtain a product of very high purity with this apparatus, the gas containing 87 to 90 per cent. of helium was compressed to 100 atmospheres. It entered the apparatus at *G*, passed through the heat-exchanging coils in *B*, thence through a second heat exchanger in *C*, where it was cooled still further by the vapour from the liquid in *C*. From this it passed through a coil immersed in the liquefied gas in *F*, and thence into the rectification column, *D*. Thence it passed up through a set of tubes in *A*, where its temperature could be lowered to approximately $-200°$ by the surrounding liquid and vapour. As shown in the diagram, the purified gas passed out through a high-pressure valve, *E*, and thence through the exchanger, *B*, to


Trap
6"x1"
E Expansion H.P. Valve
½" Union to Vacuum Pump
G From Compressor
Pipe 2 ft. x ⅛" For Depth Gauge
To Gaso. ⅜" Pipe Union
A
Hampson Interchanger
B
Brass Tube 5 Diam. ½ Thick Approx.
⅜" Union
12 Tubes 30"x¼"
Liquid A
Pipe Union ⅜" To Gasom.
Hampson Interchanger
C
Pipe 2"x⅛" For Depth Gauges
⅜" Press Tube
¼" Union
Liquid A
2 Valves & 10ft of Tube to be supplied
Tube 20"x½"
Tubes for depth gauges
F
Union
D
Coil
Tube-3" Dia. x12" long reservoir
Perforated plate on bolts
H.P. Taps
6"
From Linde Machine.
Draw off Valve H.P.
H

a gasometer, where it could be stored prior to being compressed into cylinders. All gases which were condensed in the tubes in *A* or in the column *D* could be run off at *H*. As the pressure of nitrogen is less than half an atmosphere at −200°, it was estimated that, by maintaining the gas containing 87—90 per cent. of helium at 100 atmospheres in the whole apparatus, the final product must necessarily have a purity of more than 99 per cent. As the apparatus was designed, it will be seen that it could be used, not only for obtaining a product of high purity at the works, but also for purifying helium which became contaminated with air by use in balloons in service. Through numerous delays experienced in obtaining delivery of tubing, liquefying equipment, etc., this purifying apparatus has not been given any more than a preliminary trial. From this, however, it is quite evident that it will prove satisfactory in operation. For the purpose of carrying out this scheme of high-grade purification, a liquid-air plant was installed by the University of Toronto. Motors and an electric current supply were furnished by the Hydro Electric Commission of Ontario, and a special financial grant was made by the Honorary Advisory Council for Scientific and Industrial Research of Canada to supplement that made by the Admiralty and the Air Board of Great Britain.

Final Design of Helium-extracting Apparatus.

From the foregoing it will be seen that every step in the production of high-grade helium has been carefully examined and tested. From the experience gained, we have been able to draw up specifications for a commercial plant which will enable one to treat the whole of the natural gas of the Bow Island supply in Alberta. The unit proposed will deal with about 1600 cubic metres or 56,500 cubic feet of gas per hour at normal pressure and temperature. At the altitude of Calgary, this would be equivalent to 62,200 cubic feet per hour. The machine would easily cope with 66,000 cubic feet per hour or 1100 cubic feet per minute. Of these machines, six would deal with 9,500,000 cubic feet of gas per day, and would thus take about the average daily supply available from the field, as based on records of the average yearly consumption. In order to have sufficient machines to operate regularly to capacity, it would probably be advisable to have eight helium columns included in the plant.

The cost of a commercial plant suitable for treating the whole of the supply of the Alberta field would probably be less than £150,000. The amount of helium of upwards of 97 per cent. purity obtainable per year from the field would be about 10,500,000

cubic feet. This is based on the assumption of an efficiency of 80 per cent., which experience has shown is obtainable. As to operating costs, our experience has shown that, allowing for interest on the investment, a ten years' amortisation, salaries, supplies, and running charges, helium can be produced at the Alberta field for considerably less than £10 per 1000 cubic feet. This sum does not, of course, include the cost of purchasing cylinders or of transporting them from and to the works. Neither does it include any compensation to the owners of the field for the supply of gas. The column as finally designed for the production of helium of approximately 97 per cent. purity is shown in Plate III. It is not drawn to scale, but it conforms on general lines to the standard oxygenen-nitrogen machines of L'Air Liquide Société. It consists of:

I. Two exchangers of temperature, one of which, Q, is shown, the two being so arranged that the flow of gas through them can be reversed, as is the present practice in the oxygen and nitrogen machines. The high-pressure gas is in the outer casing, and the return low-pressure gas in the small tubes; the heads are provided with three sections, so that the low temperature of the outgoing gases can be utilised.

II. A liquefier, R. This is the same as the liquefier in the standard machines, but it has only one of the returning gases flowing through it.

III. An expansion engine, S. This engine is of the standard type used in the oxygen and nitrogen machines.

IV. A first vaporiser and pot, U, T. This vaporiser, with pot for collecting liquid, is the same as on the standard nitrogen column.

V. A second vaporiser and pot, W, V. This vaporiser, with the pot, is similar to the second vaporiser now used on the standard nitrogen columns. It should be about one-third the size of the first vaporiser, U.

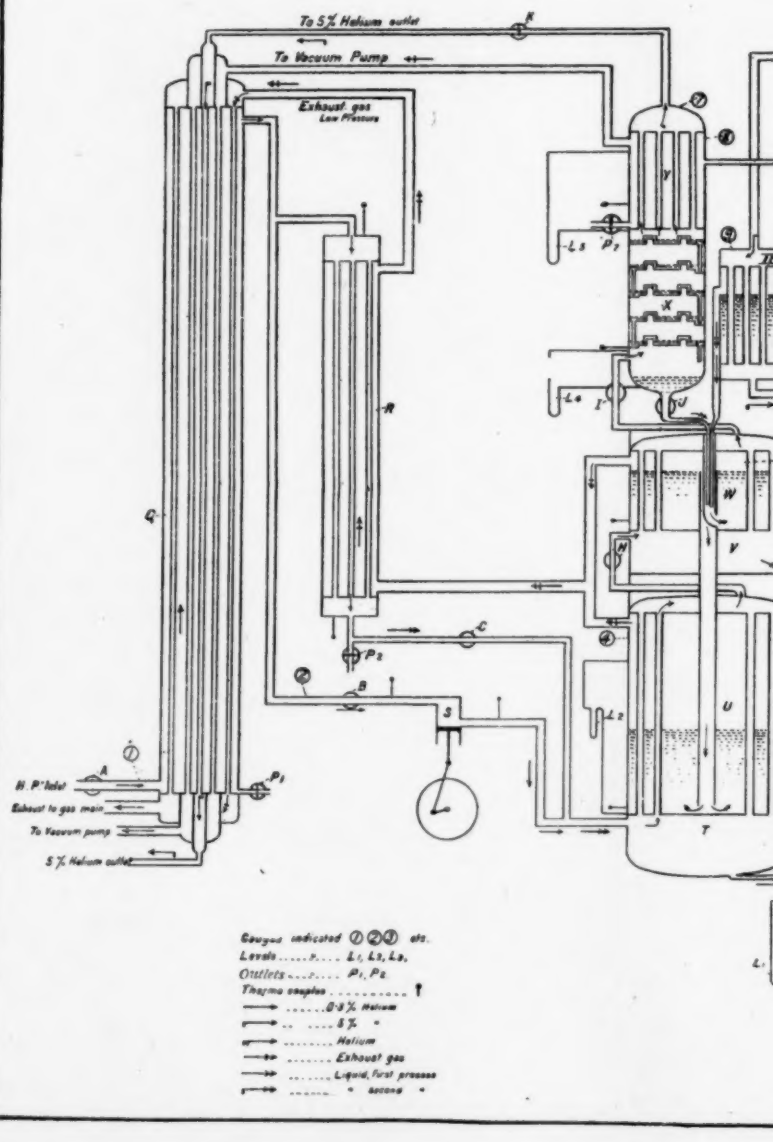
VI. A rectification column, X. This column should stand a pressure of 10 atmospheres and have a collecting basin at the bottom. Its diameter should be about three-eights of that of the vaporisers U or W. Its length should not exceed 2 feet.

VII. A vaporiser, Y. The diameter of this vaporiser is the same as that of the rectification column, X, and its length should not exceed 2 feet. On this vaporiser, a partial vacuum is maintained.

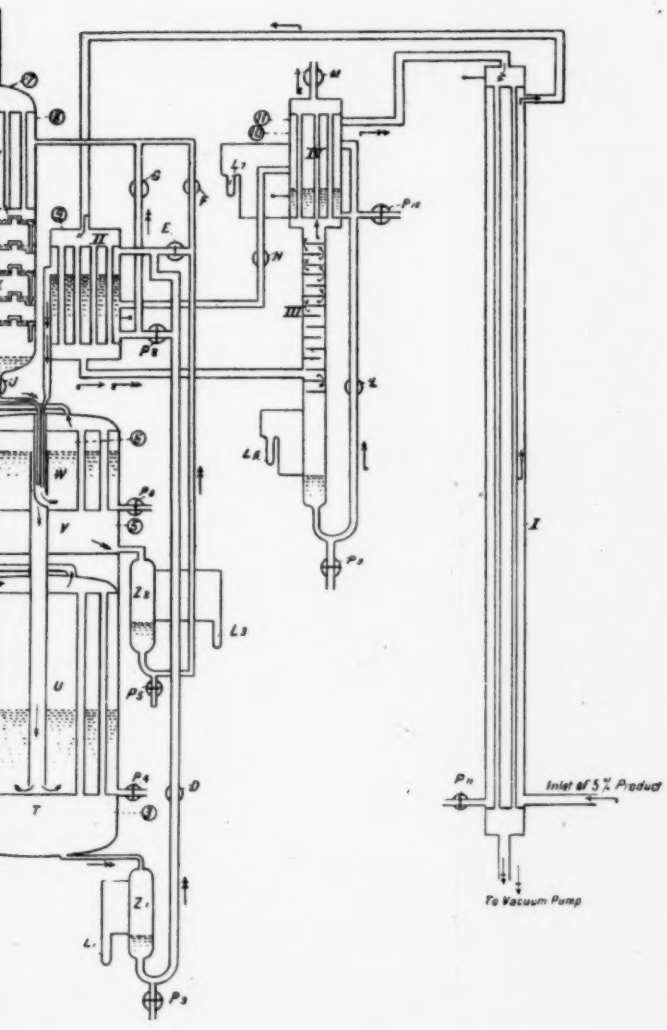
VIII. Two collecting bottles, Z_1, Z_2.

IX. Two exchangers of temperatures, one of which, I, is shown. These are similar to Q, and should be reversible, but their capacity is only 6 per cent. of Q.

HELIUM COL


To 5% Helium outlet
To Vacuum Pump
Exhaust gas
Low Pressure
H. P. Inlet
Exhaust to gas main
To Vacuum pump
5% Helium outlet
Gauges indicated ① ② ③ etc.
Levels L1, L2, L3,
Outlets P1, P2
Thermo couples .....
.....8-9% Helium
..... 5% "
..... Helium
..... Exhaust gas
..... Liquid, first process
..... " second "

COLUMN



[To face p. 934, Trans.

X. A vaporiser, *II*. This vaporiser should be of the same size as *Y*, and the high-pressure side of it should stand a pressure of 50 atmospheres.

XI. A rectification column, *III*. This column should stand a pressure of 50 atmospheres, and should be about half the diameter of the column *X* and about 3 feet long.

XII. A vaporiser, *IV*. This should be similar to vaporiser *II*, but only half the diameter; on this vaporiser a partial vacuum is maintained.

XIII. The control valves are designated by letters from *A* to *N*, fourteen in all.

XIV. The outlets are designated by P_1, P_2, etc., eleven in all.

XV. The gauges are designated by the numbers in parenthesis, thus, (1), (2), etc., eleven in all.

XVI. The levels for showing the depth of liquid are designated by L_1, L_2, etc., seven in all.

XVII. The method of connecting up is shown in the figure.

The method of using the column is as follows.

The First Process.—(*a*) The compressed gas enters the exchangers, *Q*, through valve *A*, and, after passing out of the exchanger at the top, some of it goes through the liquefier, *R*, and the rest of it through the expansion engine, *S*, to the first pot, *T*. In *T* the pressure is about 4 atmospheres, and most of the gas is liquefied in the condenser, *U*. The uncondensed part passes through the valve *H* into *V*, where more of it is liquefied in the condenser, *W*. The still uncondensed gas flows through valve *I* to the bottom of the rectification column, *X*; it passes up through the column, through the condenser *Y*, where more of it is liquefied, and the rest, which now contains about 5 per cent. of helium, passes through valve *K*, where the pressure is reduced to nearly atmospheric, and it passes through the inner section of the exchanger to a gasometer.

(*b*) The liquid that collects in the pots *T* and *V* is drained into the bottles Z_1 and Z_2, which are made fairly long, and the bottom limbs of the levels are about 6 inches from the bottom, so that it is possible always to keep liquid in the bottom of the bottles and prevent any uncondensed gas escaping. The liquids from the bottles Z_1 and Z_2 are passed through the valves *D* and *E*, respectively, into the vaporiser, *II*; in addition, the liquid from Z_2 can also be run into the vaporiser, *Y*, through valve *F*. The liquid in the vaporiser *II* overflows into the vaporiser *W*, and it overflows from *W* into the first vaporiser, *U*. Some of the liquid in the vaporiser *II* can be passed through the valve into *Y*. Liquid that condenses in *Y* flows down through the rectification

trays in *X*, and is passed through the valve *J* into the vaporiser *W*.

(*c*) The gases from the evaporating liquids in the vaporisers *U* and *W* pass directly back to the liquefier, *R*, and from the liquefier to the exchanger, *Q*, as shown in the diagram. The gas evaporated in vaporiser *II* flows with the liquid down into vaporiser *W*. The gas evaporating under vacuum in vaporiser *Y* passes out through the exchanger, *Q*, to the vacuum pump.

The Second Process.—(*d*) The gas containing helium drawn off in the first process through the valve *K* is re-compressed to 30 atmospheres, and passes through the exchanger *I* to the top of the condenser *II*; it flows down through *II*, where part of it is liquefied, and the liquid and gas pass into the rectification trays, *III*, to the collector at the bottom, the gas passing up through the column to the condenser *IV*, where the rest of the nitrogen is condensed, and the product, containing about 97 per cent. of helium, is drawn off through the valve *M*.

Notes on Special Points.

The vaporiser *Y* is the coldest part of the machine in the first process, owing to the liquid boiling under a partial vacuum. The liquid produced in the condenser runs down through the rectification trays in *X*, and the uncondensed gas from *W* passes up through it. Any helium and most of the nitrogen in the liquid will be recovered, and a large part of the methane in the gas will be condensed. Thus the product drawn off through *K* will contain very little methane.

In the second process, the gas containing 5 per cent. of helium under about 30 atmospheres pressure flows from the top to the bottom of the vaporiser *II*. This vaporiser is filled with the liquid produced in the first process, and is at the temperature of liquid methane ($-163°$). At this temperature, nitrogen condenses at about 12 atmospheres, and much of it is condensed. The liquid and gas both flow over a few trays, and the helium dissolved in the liquid would be recovered. The uncondensed gas flows up through the trays, and is cooled and partly condensed by the cold liquid from *IV*. The liquid is gradually warmed, and thus any helium in it will be recovered.

Miscellaneous Investigations.

In the course of the investigation on the development of a machine for extracting helium from natural gas, supplies of helium of varying degrees of purity became available. These were highly purified, and were used for the investigation of certain collateral

problems which demanded solution. Among the results obtained, it was found that for aeronautical purposes hydrogen could be mixed with helium to the extent of 15 per cent. without the mixture becoming inflammable or explosive in air. Mixtures containing even as much as 20 per cent. of hydrogen could be burnt or exploded only when treated in an exceptional manner. The permeability of rubbered balloon fabrics for helium was shown to be about 0·71 of its value for hydrogen. For skin-lined fabrics, the permeability to hydrogen and helium was about the same. Thin soap films were found to be about one hundred times more permeable to hydrogen and helium than rubbered balloon fabrics, but untreated cotton fabrics when wetted with distilled water were but feebly permeable to these gases. It was found that rapid estimations of the amount of helium in a gas mixture could be made with a pivoted silica balance, a Shakspear katharometer, or a Jamin interferometer.

The latent heats of methane and ethane have been determined, as has also the composition of the vapour and liquid phases of the system methane–nitrogen. It has also been shown that helium containing as much as 20 per cent. of air, oxygen, or nitrogen can be highly purified in large quantities by simply passing it at slightly above atmospheric pressure through a few tubes of cocoanut charcoal kept at the temperature of liquid air. In the spectroscopy of the ultraviolet, helium has been found to be exceptionally useful. Arcs in helium between tungsten terminals can be easily established and maintained. In a particular investigation with a vacuum grating spectrograph, it was found that by the use of arcs in helium under 30 cm. pressure, illumination could be maintained continuously for hours, and with such arcs spectra could easily be obtained extending to below 1000 A.U.

Although it is known that free electrons can exist in highly purified helium to an amount easily measurable, it was found that pure helium under a pressure of more than 80 atmospheres did not exhibit anything in the nature of metallic conduction. Moreover, the mobilities of both positive and negative ions formed by α-rays in helium under this high pressure were found to have about one-third the value expected on the basis of an inverse pressure law.*

* The following is a list of the papers which deal with the subjects mentioned: (1) "Report on some sources of Helium in the British Empire" (McLennan, *Bulletin No.* 31, *Mines Branch, Department of Mines, Canada*, 1920). (2) "The Estimation of the Helium Content of Gases by the use of a Katharometer" (Murray, *Trans. Roy. Soc., Canada*, 1919, 27). (3) "The Use of the Jamin Interferometer for the Estimation of small amounts of

The Uses of Helium.

The investigation into the problem of producing helium in large quantities was originally undertaken with a view to the utilisation of the gas in aeronautical warfare. The investigation has shown that it can be produced at a cost which is not excessive, but it has also been shown that from the sources in the Empire which are known and have been examined, the supply of helium cannot be greater than about 12,000,000 cubic feet per year. This quantity clearly would be sufficient to keep only a very few of our airships of the larger type in commission, even if the gas were diluted to the extent of 15 per cent. with hydrogen. This amount would, however, suffice to keep a number of the smaller aircraft supplied. Moreover, it might be used to fill fireproof compartments adjacent to the engines if it were ever decided to instal these within the envelopes of our larger airships.

Since it has been demonstrated that helium can be produced in quantity, one is led naturally to consider in what directions one can hope to use the gas other than that originally intended. In industry it may be used as a filling for thermionic amplifying valves of the ionisation type. It may also be used for filling tungsten incandescent filament lamps, especially for signalling purposes where rapid dimming is an essential, and for producing gas arc lamps in which tungsten terminals are used, as in the "Pointolite" type. Both of these varieties of lamps possess the defect, however, of soon becoming dull owing to the ease with which incandescent tungsten volatilises in helium, and deposits on the surface of the enclosing glass bulbs. As regards illumination, helium arc lamps possess an advantage over mercury arc lamps in that the radiation emitted has strong intensities in the red and yellow portion of the spectrum.

Helium or Hydrogen in Air" (McLennan and Elworthy, *ibid.*, p. 19). 4) "The Permeability of Balloon Fabrics to Hydrogen and Helium" (Elworthy and Murray, *ibid.*, p. 37). (5) "Composition of the Vapour and Liquid Phases of the System Methane–Nitrogen" (McTaggart and Edwards, *ibid.*, p. 57). (6) "A Continuous Flow Apparatus for the Purification of Impure Helium Mixtures" (Edwards and Elworthy, *ibid.*, p. 47). (7) "On the Combustibility of Mixtures of Hydrogen and Helium" (Satterly and Burton *ibid.*, p. 211). (8) "On the Latent Heats of Methane and Ethane" (Satterly and Patterson, *ibid.*, p. 123). (9) "On the Mobilities of Ions in Helium at High Pressures" (McLennan and Evans, *ibid.*, 1920). (10) "On the Permeability of Thin Fabrics and Films to Hydrogen and Helium" (McLennan and Shaver, *ibid.*). (11) "Spark Spectra of Various Elements in Helium in the extreme Ultra-violet" (McLennan and Lewis, *ibid.*). (12) "Arc Spectra in vacuo and Spark Spectra in Helium of Various Elements" (McLennan, Young, and Ireton, *ibid.*).

It has been shown by Nutting (*Electrician*, March, 1912) that Geissler tubes filled with helium are eminently suitable, under certain conditions, for light standards in spectrophotometry, but the amount of the gas which could be used in this way is very small.

In spectroscopy, especially for investigations in the ultra-violet region, helium is invaluable. Doubtless its use in this field will be rapidly extended. The use of the gas in physical laboratories generally, and especially where certain investigations on the properties of matter are carried out, will also be greatly increased.

It has recently been proposed to use helium in place of oil for surrounding the switches and circuit-breakers of high-tension electric transmission lines. If the gas should prove suitable for this purpose, large quantities could be utilised, but it has yet to be demonstrated (and it is not clear that it can be) that in this field helium possesses any advantage over the oils now used.

It has been suggested by Elihu Thomson and others that if divers were supplied with a mixture of oxygen and helium, the rate of expulsion of carbon dioxide from the lungs might be increased, and the period of submergence as a consequence be considerably lengthened.

It is probable, however, that in the field of low temperature research helium will immediately find its widest application. For this work, helium is unique in that, when liquefied and possibly solidified, it enables one to reach the lowest temperatures attainable. Every effort should be directed towards the exploitation of its use in this direction.

One point that is important and should not be overlooked is that the supplies of natural gas from which helium can be extracted are being rapidly used up. When our natural gas fields are depleted, it would appear that our main source of supply of helium will have disappeared. Careful consideration should, therefore, be given to the problem of producing helium in large quantities while it is still available, and of storing it up for future use. As already stated, it may be that in the future it will be of paramount importance to have even a moderate supply of the gas available.

A Cryogenic Laboratory.

To chemists and physicists especially, the discovery that helium can be produced in quantity at a moderate cost opens up a vista in the realm of low temperature research of surpassing interest. By means of liquid oxygen, the properties of substances can be studied down to a temperature of $-182{\cdot}5°$. Liquid nitrogen provides us with a temperature of $-193{\cdot}5°$, and hydrogen, which was

originally liquefied in 1898 by Sir James Dewar, enables us to reach −252·8°. It is but a few years since Onnes, after prolonged effort, secured sufficient helium to enable him to liquefy this gas too. In a brilliantly conceived research, he succeeded in accomplishing this feat in 1908, and in doing it reached a temperature within approximately 1° or 2° of the absolute zero.

The amount of liquid helium which Onnes obtained in his investigation was small, but it sufficed to enable him to show that a number of the elements possessed a remarkable "super-conductivity" at this low temperature. Mercury in particular, at the temperature of liquid helium, possessed an electrical conductivity ten million times greater than at ordinary room temperature, and currents started by induction in a coil of lead wire at the temperature of liquid helium maintained their intensity for more than an hour with but little diminution in magnitude.

The results obtained by Onnes, although limited in number, are of great importance, for they show that if liquid helium were rendered available in quantity, fundamental information of the greatest value on such problems as those connected with electrical and thermal conduction, with specific and atomic heats, with magnetism and the magnetic properties of substances, with phosphorescence, with the origin of radiation, and with atomic structure, could be obtained.

In spectroscopy, supplies of liquid helium would enable us to extend our knowledge of the fine structure of spectral lines, and thereby enable us to obtain clearer ideas regarding the electronic orbits existing in the atoms of the simpler elements. This would lead naturally to clearer views on the subject of atomic structure generally.

In other fields, too, important information could be obtained by the use of temperatures between that of liquid hydrogen and that of liquid helium. What of radioactivity? Would this property be lost by uranium, thorium, radium, and other similar elements at temperatures attainable with liquid helium? Would all chemical action cease at these temperatures? Would photochemical action disappear completely? Would photoelectric action cease or be maintained at such low temperatures?

In the fields of biological and botanical research, information on problems pressing for solution could be gained also. For example, would all life in spores and bacteria be extinguished by subjecting them to temperatures in the neighbourhood of absolute zero?

The list of problems rendered capable of attack by the use of liquid helium might be easily extended; but those cited already

will serve to show that the field is large, and that it is well worth while for us to make a special effort to secure adequate financial support for the equipment and maintenance of a cryogenic laboratory within the Empire.

It is probably beyond the ordinary resources of any university to equip and maintain such a laboratory; but the project is one which merits national and probably imperial support. It should appeal to private beneficence as well, for it is a project deserving strong and sympathetic help.

A properly equipped cryogenic laboratory should include:

(1) A liquid-air plant of large capacity.

(2) A liquid-hydrogen plant of moderate capacity.

(3) A liquid-helium plant of small capacity.

(4) Machine tools, cylinders, glass apparatus, measuring instruments, etc.

Such an equipment would probably cost more than £10,000.

For building purposes, probably an additional £10,000 or £15,000 would be required.

The staff should include one or two skilled glass-blowers, two or three mechanics and instrument makers, and two or three helpers for running the machinery. To provide this staff and meet charges for light, heat, and power, probably £3,000 a year at least would be needed.

For an administrative and technical staff, probably £2,500 would be necessary.

In addition to the above, special provision would have to be made to secure an adequate supply of helium. If industrial uses can be found for helium and a works were established in Alberta for the production of helium on a large scale, the problem of supply would be solved, for the amount of the gas which would be required for low-temperature research would probably not be more than 20,000 or 30,000 cubic feet a year. In default of a production-works on a large scale being established, it would be necessary to instal a small plant at Calgary for the specific purpose of supplying the cryogenic laboratory with helium. This could easily be done at the present time, as the experimental plant is still in situ. It would require from £3,000 to £4,000 to make the changes in the plant which experience has shown are necessary and to provide the additional auxiliary machinery, tools, etc., required.

If this plant were run for three or four months each year, an adequate supply of helium could be obtained. The expense of running the plant under these conditions would be high, and it would probably be found that it would require from £2,000 to

£3,000 to operate it for a period of three or four months each year. This amount would, of course, have to cover charges for salary of staff, compensation to the owners of the natural gas, light, power, miscellaneous supplies, freight charges on cylinders, etc.

From the above it will be seen that a scheme such as that outlined would require in the aggregate a capital expenditure of about £30,000 for buildings and plant, and the interest on an endowment of about £125,000 for operating and maintaining the cryogenic laboratory together with the supply station.

If a cryogenic laboratory, with its auxiliary supply station, were established along the lines indicated, it would probably be found to be more economical to run the supply station continuously for a number of years, and to store for future use the helium accumulated. In this connexion it should be stated that the experimental plant as it exists would probably not produce more than 100,000 cubic feet of helium per year. The plant could, however, be easily manifolded, and the Governments of Great Britain and Canada might, from the point of view of national safety, legitimately be asked to assume responsibility for operating it.

Much of our knowledge acquired in the field of low temperature research we owe to the brilliant work of such distinguished men as Andrews, Davy, Faraday, and Dewar. The discovery of the rare gases, helium, neon, argon, krypton, and xenon, we owe to Rayleigh, Ramsay, and Dewar. How could we more fittingly perpetuate the work of these great men than by establishing on a permanent basis a cryogenic laboratory for the purpose of making still further progress in the field of low-temperature research—a field in which British scientists have made such brilliant and notable advances?

In conclusion, it should be stated that whilst the investigation just described was financed by the British Admiralty, and in its later stages by the British Air Ministry, valuable assistance was given by L'Air Liquide Société of Paris and Toronto, by the Canadian Pacific Railway Co. of Canada, by the Hydro-Electric Commission of Ontario, and by the University of Toronto. In carrying out the collateral investigations, valuable help was given by Professors E. F. Burton, J. Satterly, H. F. Dawes, and H. A. McTaggart. To Mr. J. Patterson, M.A., whose services were lent by the Director of the Meteorological Office of Canada, much credit is due for working out details of design and construction in connexion with the production of the rectifying column. Mention should also be made of the creditable manner in which the

experimental plant was handled during the trial runs made between December 1st, 1919, and April 17th, 1920, by Mr. R. J. Lang, assisted by Mr. D. S. Ainslie and Mr. H. R. Foreman.

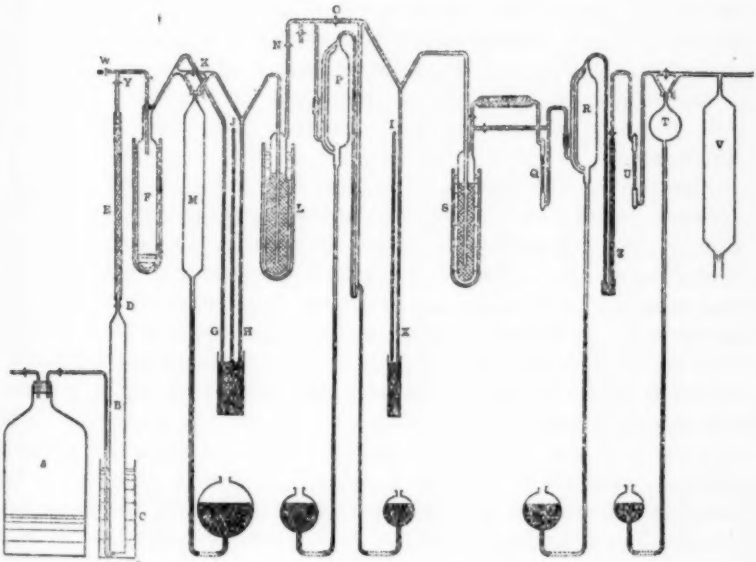
APPENDIX A.

Determinations of Helium Content of Natural Gases.

In determining the helium content of a sample of natural gas, the following procedure was adopted, and the apparatus used is shown in Fig. 2.

A is a glass bottle in which the gas was brought from the field. The gas was forced from *A* into the glass tube *B*, where it collected

FIG. 2.



by water displacement. The capacity of *B* was adjusted to be 1200 c.c. under ordinary conditions of temperature and pressure. The gas was introduced into the apparatus in units of this volume. Before commencing the analysis the charcoal tubes were strongly heated by electric heaters to about 300° to expel absorbed gases, and the whole of the apparatus to the right of the tap was carefully exhausted. All the taps were then turned off. The charcoal on cooling absorbed the remainder of the gas in apparatus, and a good vacuum resulted.

On turning the taps *D* and *Y*, the gas flowed from *B* through a drying tube *E* containing calcium chloride into the condenser *F* of about 400 c.c. capacity, which was immersed in liquid air kept in a Dewar's tube. Condensation of the hydrocarbons occurred at once, the liquid air boiling off rapidly. Comparison of the manometer *G* with the barometer *J* gave the pressure of the uncondensed gases in *F* plus the vapour pressure of the condensed gases.

Usually *B* was filled and emptied five times in quick succession, so that the first charge in *F* was 6000 c.c. of natural gas. After some minutes when the liquid air had ceased from boiling and the manometer was at rest the pressure in *F* was read. Subtracting from this reading the vapour pressure of methane at the temperature of liquid air, we get the pressure of the uncondensable gases in *F*, and knowing the volume of *F* it is an easy matter to find approximately the percentage of uncondensable gases in the sample of natural gas. This analysis, rough though it was, gave useful information as to the suitability of the natural gas for the manufacture of helium on a large scale.

Meanwhile, the tube *L*, of about 300 c.c. capacity, which was full of finely broken cocoanut charcoal, had been immersed in liquid air.

The tap *K* was then opened and the uncondensed gas shared between *F* and *L*. The mercury in the gauge rose quickly, and the liquid air surrounding *L* boiled vigorously, indicating a rapid evolution of heat when the gases are absorbed by charcoal. This was especially noticeable the first time the charcoal was used after being heated. When the gauges were nearly at the same level, *K* was closed, and the remainder of the uncondensed gas in *F* transferred to *L* by means of the large mercury pump *M*. This pump was simply a long wide tube with a two-way tap at the top and a flexible tube and mercury reservoir at the bottom. It was very efficient, and after about five strokes practically all the gas had been transferred to *L*, the pressure in *F* falling to about 3 or 4 cm. The transfer of the gas was especially complete, since at each expansion of the matter in *F* some of the liquid methane would evaporate and sweep out the gas; an excess of pumping is detrimental, as it only transfers methane to *L*, thus tending to clog the charcoal. On standing, the pressure in *L* slowly decreased as absorption reached its maximum amount. Usually, very little except the helium was left unabsorbed in this tube.

When the reading of the gauge *H* was steady, the taps *N* and *O* were opened and the unabsorbed gas was allowed to diffuse over to a second charcoal tube *S* of about 200 c.c. capacity, which was also cooled in liquid air. The tap *O* was then closed, and com-

plete transference of the gas was effected by a mercury pump P of special design. In the early days of the experiment the pump in this position was of the same type as M, but the working and cleaning of the two-way tap proved inconvenient, and it was replaced by the pump shown.

While these operations had been going on any gas left in the apparatus between taps above S and the delivery tube was completely pumped out by the pump R, exhaustion being carried to such an extent that the electric charge had great difficulty in passing through the tube Q.

The gas having remained in the second charcoal tube S for some time and the gauge X attached to this tube having become steady, the taps above S were opened and the gas was pumped through the discharge tube and delivered to the collector Z, which was improvised from a graduated eudiometer by the placing of a tap at the closed end. The phosphoric oxide tube placed to the right of S was only required in the early stages of the experiment, when the charcoal gave off water on heating. A by-pass was placed in between S and the pump R to facilitate the action of the pump.

Before the gas was pumped off, its spectrum was carefully examined by a small, direct-vision spectroscope, and if any but the lines of helium (and mercury) were found, the gas was returned to the charcoal tube, or, in the case of great impurity, exhausted to the air and a fresh start made on a smaller quantity of the original gas. For example, if the natural gas contained large quantities of nitrogen and hydrogen, these may escape absorption, and their presence would be detected at this stage.

The gas obtained in the collector Z was invariably pure helium, and from the readings of its volume and pressure, the volume at atmospheric pressure was calculated.

Tubes similar to V were used for storage, and the pump T was designed to transfer the helium collected in Z over to V until the latter was filled at atmospheric pressure. The tube and pump had previously been exhausted by a mercury pump and a charcoal tube in liquid air (not shown in the figure), and then sealed off just to the right of V.

In making accurate determinations of the helium content of a natural gas, it was found necessary to use, for displacement purposes only, water which had been freed by boiling from occluded air and other gases. Ordinary tap-water or water from rivers was generally found to contain sufficient quantities of air to invalidate the determinations if high accuracy was demanded.

APPENDIX B.

Density Determinations by Balance Method.

For rapid and accurate determinations of gas density, the use of a delicately pivoted silica balance was found to be invaluable. This type of balance was originally designed and used by Aston

FIG. 3.

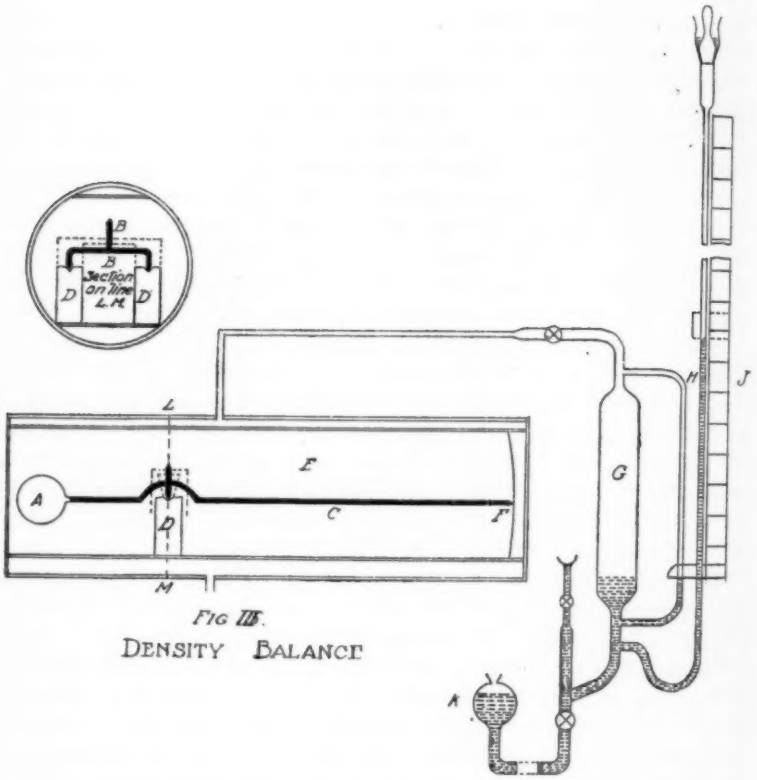


FIG III.
DENSITY BALANCE

(*Proc. Roy. Soc.*, 1913, [*A*], **89**, 439). A quartz micro-balance of exceedingly high sensitivity had been designed by Steele and Grant (*ibid.*, 1909, [*A*], **82**, 580), and used by Gray and Ramsay (*ibid.*, 1910, **84**, 536) at an earlier date, and Taylor (*Physical Rev.*, 1917, [N.S.], **10**, 653) has recently published an account of a form of the instrument which enabled him to determine with great exactness the density of helium. Aston's form of the instrument was, however, found to be the most suitable for our purposes. One

method of using the instrument has been described already by R. T. Elworthy (*Bulletin No.* 31, *Mines Branch, Dept. of Mines, Canada*, 1920), and a second, which has been found very useful, has been worked out for the present investigation by Mr. John Patterson, M.A. It is shown in Fig. 3.

The density balance consisted of a quartz bulb, *A*, 1·25 cm. in diameter, and an arm, *C*, about 10 cm. long, mounted on a rocking arm, *B*. The two points of this arm rested on jewels, and the arm had a protecting case around it, as shown by the dotted lines, so as to prevent the balance from getting out of the jewels. The end of the arm, *C*, was turned at right angles and moved along a scale, which could be easily read to 0·1 mm. In most forms of this instrument, the pressure in the density chamber is adjusted by either exhausting or admitting the gas very slowly until the correct pressure is obtained. This is usually a very troublesome operation, and to overcome it, a reservoir, *G*, was attached to the chamber, which permitted the pressure to be altered by simply raising or lowering the mercury reservoir. The reservoir was provided with a manometer, *H*, with a scale, the zero of which could be set on the lower limb of the manometer and the pressure read directly to 0·1 mm. The manometer, *H*, could be used either for pressures less than atmospheric, in which case the tube, *H*, was free of air, or for pressures greater than an atmosphere, when the seal at the top is taken out. The balance could be calibrated for a standard gas, such as air, by plotting pressures against the scale reading. Then, to obtain the density of a gas, all that was necessary was to wash out the density chamber thoroughly and take two or three readings at different parts of the scale. From these, the relative density could be determined at once. It was not necessary by this method to adjust the pressure until the indicating point was at a fixed position. A reading correct to two decimal places could be obtained with this instrument in about five minutes. The temperature of the air used for calibrating the balance should, of course, be known, and then, if the other determinations were made at a different temperature, a correction could be applied.

CIV.—*Some New Derivatives of Mesitylene and ψ-Cumene.*

By Charles Stanley Gibson.

The investigation of the chemical constituents of certain fractions of Edeleanu oil obtained from Borneo petroleum (compare Jones and Wootton, T., 1907, **91**, 1148) has led to the isolation of hitherto undescribed derivatives of mesitylene and ψ-cumene. As very little information concerning the chemical behaviour of these hydrocarbons is contained in the literature, it is considered desirable to describe the work which has now been done on these substances.

The most interesting of the new compounds described in the present communication are the dinitro-sulphonic acids of mesitylene and ψ-cumene, together with their reduction products. Rose (*Annalen*, 1872, **164**, 65) obtained a mononitro-sulphonic acid of mesitylene, $C_6HMe_3(NO_2)\cdot SO_3H,1\frac{1}{2}H_2O$, by dissolving mesitylene-sulphonic acid in well cooled fuming nitric acid. He also described certain of its salts, and this appears to be the only nitro-sulphonic acid of mesitylene hitherto known. No nitro-sulphonic acid of ψ-cumene appears to have been described previously.

The reduction of *dinitromesitylenesulphonic acid* under the condition described in the paper leads to the formation of a *diamino-mesitylenesulphonic acid*; whereas the reduction of a *dinitro-ψ-cumene-5-sulphonic acid* leads to the formation of a *mononitro-monoamino-ψ-cumene-5-sulphonic acid* and also the fully reduced compound, *diamino-ψ-cumene-5-sulphonic acid*. The nitroamino-ψ-cumene-5-sulphonic acid is formed when the reduction of the dinitro-acid is not carried to completion. When the reduction of dinitromesitylenesulphonic acid is not carried to completion, the diamino-sulphonic acid is formed and unchanged dinitro-sulphonic acid is left. From a comparison of the formulæ of dinitromesitylene-sulphonic acid and dinitro-ψ-cumene-5-sulphonic acid, and from the fact that the former does not appear to yield easily a half-reduced acid, it appears that the constitution of the mononitromonoamino-ψ-cumene-5-sulphonic acid is most likely 6-nitro-3-amino-2:4:5-trimethylbenzenesulphonic acid.

For the investigation considerable quantities of mesitylenesulphonic acid and of ψ-cumene-5-sulphonic acid were necessary, and methods of preparation of these compounds somewhat more convenient than those previously described (Jacobsen, *Annalen*, 1868, **146**, 95) have been devised.

Experimental.

Preparation of Mesitylenesulphonic Acid.

To determine how far the method of sulphonation adopted was successful, the sulphonation product of the hydrocarbon was isolated as the sodium salt. The pure hydrocarbon (85 c.c.) was stirred at 55°, and 85 c.c. of sulphuric acid (D 1·84) run in fairly rapidly and the whole kept at 55° during two hours. The mixture was diluted with water and treated at 90° with lime in quantity sufficient to neutralise the excess of sulphuric acid, and with sodium carbonate to neutralise the sulphonic acid. After filtering from the calcium sulphate, the solution was evaporated, and the sodium salt of mesitylenesulphonic acid was obtained in almost quantitative yield. It is conveniently recrystallised from boiling water.

The almost pure acid is most conveniently obtained directly by allowing the sulphonated mixture to cool and adding a weight of ice equal to that of the sulphuric acid used. On keeping, mesitylenesulphonic acid crystallises out in theoretical quantity. It is filtered on cloth and dried on porous plate in a desiccator.

The mesitylenesulphonic acid and its sodium salt were identified by conversion into the sulphonyl chloride and sulphonamide in the usual manner. Mesitylenesulphonyl chloride when recrystallised from a mixture of benzene and light petroleum was obtained in colourless, massive prisms, melting at 56—57°, and mesitylenesulphonamide, recrystallised from aqueous alcohol, was obtained in colourless needles melting at 144°. The latter melting point is somewhat higher than that given by Jacobsen (*Annalen*, 1876, **184**, 157).

Dinitromesitylenesulphonic Acid, $C_6Me_3(NO_2)_2 \cdot SO_3H, 4H_2O$.

This acid may be prepared either from mesitylenesulphonic acid isolated in the way described above or directly from the hydrocarbon. In preparing it from the sulphonic acid, 60 grams are added gradually with stirring to 72 c.c. of concentrated sulphuric acid (D 1·84). Very little rise of temperature takes place, and this operation is performed at the ordinary temperature. The sulphonic acid does not dissolve completely. The mixture is cooled in ice, the stirring continued, and a mixture of 45 c.c. of nitric acid (D 1·4) and 45 c.c. of concentrated sulphuric acid (D 1·84) is added during about two hours. The temperature at the beginning should not be more than 10°, and this gradually rises to about 35° and then begins to fall. The ice-bath is then removed, and the addition of the nitrating acid continued at the ordinary

temperature. The temperature rises to about 40° and then fall again. At this point the mixture is heated to 60°. The time fo the nitration is four hours, and the nitrating acid is run in durin about two hours.

The above quantity of nitric acid allows a 25 per cent. excess ove the two molecules of nitric acid necessary for the reaction, an before all the nitrating acid has been run in, the colour of the mix ture becomes very much paler and solid begins to separate. Whe the nitration is finished, the mixture is allowed to cool and poure on 250 grams of ice and then stirred until no more nitrous fume are evolved. The crystalline acid is collected, and may be purifie either by crystallisation from a small quantity of hot water, or b dissolving in water and adding half the volume of concentrate sulphuric acid, cooling in ice-water. The solution of the aci should be filtered from the small quantity of trinitromesitylen (m. p. 232—233°), amounting to not more than 4 grams. Th yield of the acid is rather more than 90 per cent. of the theoretic quantity.

An almost theoretical yield of dinitromesitylenesulphonic aci can be obtained directly from mesitylene. Sixty grams o mesitylene are sulphonated with 69 c.c. of concentrated sulphur acid (D 1·84) under the conditions described above, and, after th sulphonation is completed, the mixture is cooled in water and th stirring continued while 81 c.c. of concentrated sulphuric acid a added during half an hour. The mixture is then cooled in ice, an the nitrating acid, 60 c.c. of nitric acid mixed with 60 c.c. of co centrated sulphuric acid of the same strengths as before, is adde under precisely the same conditions as in the case of the previo preparation. It was found that 5 per cent. of the hydrocarbon converted into the trinitro-compound; apart from this the yield o the acid is theoretical.

Dinitromesitylenesulphonic acid crystallises from its concentrate solution in hot water in large, very pale yellow plates; it contai four molecules of water of crystallisation, but slight decompositio sets in on heating before all the water of crystallisation is expelle (Found, by titration with barium hydroxide solution, M.W. = 357· 359·9; $H_2O = 20·9$.* $C_9H_{10}O_7N_2S,4H_2O$ requires M.W. = 362·5 $H_2O = 19·9$ per cent.).

Dinitromesitylenesulphonyl Chloride, $C_6Me_3(NO_2)_2·SO_2Cl$.

This is prepared in the usual way from the almost anhydro acid by the action of phosphorus pentachloride. It is readil soluble in benzene, but much less so in light petroleum. It is co

* Decomposition had set in.

veniently recrystallised from benzene containing half its volume of light petroleum. It is obtained in almost colourless, long, soft needles melting at 169—170° (Found: C = 34·9; H = 3·12. $C_9H_9O_6N_2ClS$ requires C = 35·0; H = 2·94 per cent.).

Dinitromesitylenesulphonamide, $C_6Me_3(NO_2)_2 \cdot SO_2 \cdot NH_2$.

This derivative is prepared by the action of concentrated ammonia solution on the acid chloride. On crystallisation from hot alcohol, in which it is readily soluble, it is obtained in long, silky needles melting at 228—229° (Found: C = 37·6; H = 3·88. $C_9H_{11}O_6N_3S$ requires C = 37·4; H = 3·83 per cent.).

Salts of Dinitromesitylenesulphonic Acid.

Sodium Salt, $C_6Me_3(NO_2)_2 \cdot SO_3Na,4H_2O$.—This salt was obtained from the acid by accurate titration with standard sodium hydroxide solution. It was crystallised three times from water, in which it is very readily soluble. The salt appears to be dimorphous. On allowing the concentrated aqueous solution to remain, extremely soluble, colourless, flat plates separate. On long keeping or on stirring, these change into colourless, silky needles which are much less readily soluble than the plates. It is impossible to collect the plates in the ordinary way, as they change spontaneously in the air into what appears to be the other modification. The change from one form into the other can be readily observed under the microscope (Found: H_2O = 18·85. $C_9H_9O_7N_2SNa,4H_2O$ requires H_2O = 18·76 per cent. Found: Na = 7·50. $C_9H_9O_7N_2SNa$ requires Na = 7·36 per cent.).

Ammonium Salt, $C_6Me_3(NO_2)_2 \cdot SO_3 \cdot NH_4$.—This salt is easily obtained by the action of ammonia solution on the acid. It can be recrystallised from water, and when the aqueous salt is allowed to evaporate spontaneously, the salt is obtained in colourless, thin plates. On drying in air the substance is anhydrous (Found, by titration with N/10-sodium hydroxide, NH_4 = 6·0, 6·0. $C_9H_{13}O_7N_3S$ requires NH_4 = 5·9 per cent.).

The *calcium salt*, $[C_6Me_3(NO_2)_2SO_3]_2Ca,3H_2O$, is prepared by the action of calcium carbonate on the acid, and can be crystallised from water, in which it is readily soluble. The salt is deposited from its aqueous solution in colourless prisms, which effloresce in air. The crystalline substance loses the whole of its water of crystallisation on keeping in a vacuum over concentrated sulphuric acid. The water of crystallisation was determined by allowing the substance to attain constant weight over sulphuric acid in a vacuum (Found: H_2O = 8·04. $C_{18}H_{18}O_{14}N_4S_2Ca,3H_2O$ requires H_2O = 8·04 per cent.

Found: Ca = 6·54, 6·47. $C_{18}H_{18}O_{14}N_4S_2Ca$ requires Ca = 6·48 per cent.).

Barium Salt, $[C_6Me_3(NO_2)_2SO_3]_2Ba,3\frac{1}{2}H_2O$.—This was obtained in a precisely similar way to the calcium salt. It is readily soluble in water, from which it was twice recrystallised. In appearance it is very similar to the calcium salt (Found: H_2O = 8·35; Ba = 17·64; N = 7·1, 7·2. $C_{18}H_{18}O_{14}N_4S_2Ba,3\frac{1}{2}H_2O$ requires H_2O = 8·1; Ba = 17·65; N = 7·2 per cent.).

Of the other salts of dinitromesitylenesulphonic acid, the *magnesium* salt is worth mentioning. It can be obtained by precipitation, using a soluble magnesium salt and a soluble salt of the acid. Although the salt has not been further investigated yet, it was at once seen that it is much less readily soluble than the corresponding salt of dinitro-ψ-cumene-5-sulphonic acid, and this fact has often been made use of in testing for the presence of the mesitylene acid.

Diaminomesitylenesulphonic Acid, $C_6Me_3(NH_2)_2{\cdot}SO_3H$.

The reduction of dinitromesitylenesulphonic acid can be successfully carried out by the usual methods. In most of the experiments iron and a minimum quantity of acetic acid have been used, but the reduction by means of ferrous carbonate has also been found satisfactory. Two typical experiments may be described.

Ten grams of the dinitro-acid are exactly neutralised with *N*-sodium hydroxide solution, and water is added until the volume of the solution is about 100 c.c. Twenty grams of cleaned and ground iron borings are placed in a round bottomed flask provided with an air condenser; 30 c.c. of water and 1 c.c. of glacial acetic acid are poured into the flask and allowed to boil gently for about twenty minutes. After this time the boiling solution of the sodium dinitrosulphonate is added slowly from the top of the condenser. The flask is shaken from time to time, and when all the solution has been added, the whole is allowed to boil gently for about one and a-half hours. The most convenient way to obtain the pure acid at once is to add sodium hydroxide equivalent to the acetic acid used for the reduction, and filter the hot solution and wash the residue with a little water. To the filtrate and washings is added hydrochloric acid equivalent to the original dinitro-acid and to the sodium hydroxide added before filtering. The yield is 100 per cent.

Twenty-one grams of dinitromesitylenesulphonic acid are treated with the calculated quantity of standard sodium hydroxide solution, and dissolved in a boiling solution of 77 grams of anhydrous sodium carbonate dissolved in 250 c.c. of water. To the boiling solution is

added slowly 200 grams of crystallised ferrous sulphate dissolved in a litre of water. The mixture is kept boiling and stirred continuously. As soon as all the ferrous sulphate solution has been added, the solution is filtered while still hot, and the filtrate evaporated and then acidified with hydrochloric acid equivalent to the amount of dinitro-acid originally taken. The diamino-acid is at once precipitated in almost theoretical quantity, and is practically pure.

Diaminomesitylenesulphonic acid, obtained in either of the above ways, is a colourless, microcrystalline substance insoluble in all the usual organic solvents, including acetic acid. It decomposes without melting. For most purposes it is unnecessary to purify the acid as obtained in the ways described above. For analysis it was purified by dissolving in sodium hydroxide solution, filtering, and adding hydrochloric acid equivalent to the alkali hydroxide. The acid was then washed with warm water (Found: C = 47·0; H = 6·18. $C_9H_{14}O_3N_2S$ requires C = 46·9; H = 6·13 per cent.).

Sulphonation of ψ-Cumene.

ψ-Cumene is conveniently sulphonated to ψ-cumene-5-sulphonic acid under precisely the same conditions as those described above for the preparation of mesitylenesulphonic acid. The yield is quantitative. It should, however, be observed that the whole of the sulphonic acid is not precipitated on dilution, as is the case with mesitylenesulphonic acid, only 75 per cent. of the sulphonic acid being so obtained. The remainder may be conveniently isolated as the calcium salt.

ψ-Cumene-5-sulphonic acid and its calcium salt were identified by converting them into the acid chloride and amide. Quantitative yields of these derivatives were obtained in the usual manner. ψ-Cumene-5-sulphonyl chloride crystallised from light petroleum ether in large, colourless prisms melting at 62°, and ψ-cumene-5-sulphonamide, prepared from the chloride and crystallised from alcohol, was obtained in colourless needles melting at 180—181°.

Dinitro-ψ-cumene-5-sulphonic Acid, $C_6Me_3(NO_2)_2SO_3H,4H_2O$.

The isolation of this acid is not quite so easy as that of the corresponding mesitylene compound. As in the former case, it may be prepared either from ψ-cumene-5-sulphonic acid or from the hydrocarbon itself. For the purpose of this investigation the acid was generally prepared from the hydrocarbon.

Sixty grams of ψ-cumene were sulphonated under the conditions described above, and the sulphonation mixture, while still being

stirred, was mixed during half an hour with 81 c.c. of concentrated sulphuric acid. To this mixture, cooled in ice, was added a mixture of 60 c.c. of nitric acid (D 1·48, that is, 78 grams of HNO_3 instead of the theoretical quantity, 63 grams) and 60 c.c. of concentrated sulphuric acid during two and a-half hours, and the whole stirred for a further two and a-half hours. By this time the mixture had thickened considerably, and by pouring on 540 grams of ice, 40 grams of the acid were precipitated. The filtrate was then treated with an equal volume of hot brine and allowed to crystallise slowly, when the sodium salt was deposited in fairly pure condition. It may be washed with brine, in which it is almost insoluble. The total yield of the dinitro-sulphonic acid and of its sodium salt is 80 per cent. of the theoretical.

A very convenient method of working up the nitration product was to dilute the nitration mixture, then add sodium hydroxide equivalent to the amount of hydrocarbon taken, and completely neutralise with calcium hydroxide at 90°. After filtering from the calcium sulphate and concentrating the filtrate to crystallisation, the sodium salt was obtained. When it was desired to obtain the pure acid in maximum quantity, the nitration mixture was completely neutralised with calcium hydroxide, and the calcium salt isolated in the usual manner, from which the acid was easily obtained.

Dinitro-ψ-cumene-5-sulphonic acid may be conveniently recrystallised from dilute hydrochloric acid, and is easily obtained pure. It crystallises in almost colourless, glistening, radiating crystals, which contain four molecules of water of crystallisation (Found: C = 30·4; H = 4·93, NO_2, from $SnCl_2$ required for reduction, = 25·1; M.W., by titration with $N/10$-NaOH, = 363·8. $C_9H_{10}O_7N_2S,4H_2O$ requires C = 29·8; H = 5·01; NO_2 = 25·4 per cent. M.W. = 362·3).

The preparation of dinitro-ψ-cumene-5-sulphonic acid from ψ-cumene-5-sulphonic acid is carried out under the same conditions as those for the preparation of dinitromesitylenesulphonic acid from the corresponding compound. It is necessary, however, to bear in mind that only part of the product is obtained as the crystalline acid, and that the remainder must be isolated as the sodium or calcium salt under the conditions described above. During the nitration of either ψ-cumene or of ψ-cumene-5-sulphonic acid, a small quantity of trinitro-ψ-cumene is always formed. This was identified by recrystallising from alcohol, when it separated in very pale yellow needles, melting at 185°.

Dinitro-ψ-cumene-5-sulphonyl Chloride and 5-Sulphonamide, $C_6Me_3(NO_2)_2 \cdot SO_2Cl$ and $C_6Me_3(NO_2)_2 \cdot SO_2 \cdot NH_2$.

These derivatives are obtained from the acid or the sodium salt in the usual manner.

The *chloride* crystallises from hot benzene in hard nodules. It is somewhat difficult to obtain quite free from a slight brown colour. It melts and decomposes at 190—191°.

The *amide* is readily soluble in hot alcohol, and crystallises from this solvent in small, glistening needles, which usually have a slight brown colour on cooling. It melts and blackens at 244—245° (Found: C = 37·6; H = 4·02. $C_9H_{11}O_6N_3S$ requires C = 37·4; H = 3·83 per cent.).

Salts of Dinitro-ψ-cumene-5-sulphonic Acid.

Sodium Salt.—This is prepared in the way described above or by neutralisation of the acid with standard sodium hydroxide. It is obtained in colourless nodules, which are readily soluble in hot water and somewhat sparingly so in the cold solvent. The salt gradually loses water on keeping in the air (Found, after twenty-four hours, N = 7·54. $C_9H_9O_7N_2SNa,3H_2O$ requires N = 7·65 per cent. After one week, loss = 6·84, 6·51. $C_9H_9O_7N_2SNa,1H_2O$ requires 5·45 per cent.).

It thus appears that the substance after remaining for some time in ordinary air contains rather more than one molecule of water of crystallisation. The anhydrous salt was analysed (Found: Na = 7·13. $C_9H_9O_7N_2SNa$ requires Na = 7·36 per cent.).

Magnesium Salt, $[C_6Me_3(NO_2)_2SO_3]_2Mg,4H_2O$.—This salt, which is much more readily soluble than the corresponding salt of dinitromesitylenesulphonic acid, may be conveniently obtained by adding a saturated solution of magnesium sulphate to the diluted solution produced in the preparation of the acid. After two recrystallisations from its concentrated aqueous solutions, it is obtained in pale yellow, small needles (Found: H_2O = 10·77; N = 7·9; MgO = 3·42. $C_{18}H_{18}O_{14}N_4S_2Mg,4H_2O$ requires H_2O = 10·68; N = 8·3; MgO = 3·60 per cent.).

Barium Salt, $[C_6Me_3(NO_2)_2SO_3]_2Ba,4H_2O$.—This salt was prepared by adding a solution of barium chloride to a neutral solution of the ammonium salt. The salt was at once precipitated, and after being washed free from excess of barium chloride formed small, colourless needles (Found: H_2O = 9·1; N = 7·2; Ba = 17·4. $C_{18}H_{18}O_{14}N_4S_2Ba,4H_2O$ requires H_2O = 9·15; N_2 = 7·1; Ba = 17·4 per cent.).

Diamino-ψ-cumene-5-sulphonic Acid, $C_6Me_3(NH_2)_2 \cdot SO_3H$.

This acid is prepared from the corresponding dinitro-acid most conveniently by reduction with iron and acetic acid, as described for the preparaton of diaminomesitylenesulphonic acid. The yield obtained was 93 per cent. of the theoretical. Like the mesitylene acid it is practically insoluble in all the usual organic solvents, including acetic acid. It decomposes without melting. Unlike the mesitylene acid it has been found impossible to obtain the acid free from colour; even after the most careful purification it still possesses a slight red colour, but analysis showed that the acid was pure (Found: C=46·7; H=6·30. $C_9H_{14}O_3N_2S$ requires C=46·9; H=6·13 per cent.).

Nitroamino-ψ-cumene-5-sulphonic Acid, $C_6Me_3(NO_2)(NH_2) \cdot SO_3H$.

During the reduction of the neutral solution of the dinitro-sulphonic acid prepared from Edeleanu oil by means of iron and acetic acid it was found that, on isolation of the reduction product in the usual way, a portion was identical with diamino-ψ-cumene-5-sulphonic acid and, of course, insoluble in water, whilst a smaller portion was found to be capable of recrystallisation from hot water and not identical with any of the amino- or nitro-acids previously described. Further, indications of the formation of a new acid were obtained during the estimation of the amount of dinitro-sulphonic acids in solution by means of stannous chloride solution. It was therefore determined to try the effect of reducing sodium dinitro-ψ-cumene-5-sulphonate by means of stannous chloride in quantity calculated to produce a mononitromonoamino-sulphonic acid. In these circumstances an almost theoretical amount of what is probably 6-nitro-3-amino-2:4:5-trimethylbenzenesulphonic acid was obtained.

Sodium dinitro-ψ-cumene-5-sulphonate (6·2 grams) was heated in an atmosphere of carbon dioxide with 50 c.c. of a solution of stannous chloride made by dissolving 263 grams of crystallised stannous chloride in 130 c.c. of concentrated hydrochloric acid and making up to one litre. After titration with standard iodine solution it was found that 6 grams of anhydrous sodium salt required 54·5 c.c. of the above stannous chloride solution for reduction to a mono-amino-acid. The reduction was effected in a flask which was heated during two hours in a water-bath. The product was strongly acidified with concentrated hydrochloric acid, and, after cooling, the material was collected and crystallised from boiling water, in which it is readily soluble, but it is sparingly soluble in the cold.

It crystallises in yellowish-brown needles which have no melting point (Found: C=41·4; H=4·56. $C_9H_{12}O_5N_2S$ requires C=41·5; H=4·65 per cent.). Work on the above and other derivatives of mesitylene and ψ-cumene is being continued.

The above work was carried out in the University Chemical Laboratory, Cambridge, and I wish to record my thanks to Professor Sir William Pope, F.R.S., for placing much of the material employed at my disposal and for his advice and help. I have also to express my thanks to the Directors of the Asiatic Petroleum Company for their permission to publish the work.

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CV.—*Studies on Hypophosphorous Acid. Part I. Its Ionisation Equilibria.*

By ALEC DUNCAN MITCHELL.

In the course of some investigations on the velocity of various reductions by means of hypophosphorous acid, it was found that the reactions were catalysed by hydrogen ions; and as these reactions involved the production of mineral acids, such as hydrochloric and hydriodic acids, it was decided to investigate the ionisation of hypophosphorous acid in the presence of hydrochloric acid, in order to obtain data for more precise mathematical analysis of the reactions in question.

Although the catalysis of methyl acetate is in some respects an inferior method to those involving conductivity or hydrogen-ion potential methods for problems of this nature, yet it was chosen in this case as being more comparable with the catalytic reactions concerned. Moreover, one of the chief disadvantages of the method, namely, the slight uncertainty as to the effect of neutral molecules, has been overcome to a large extent by the method of calculating the results.

Many empirical formulæ have been advanced, from time to time, to connect the degree of ionisation of "strong" acids with the dilution in such a way as to give a constant analogous to that obtained for weak acids by Ostwald, but none of these is capable of predicting the equilibria which obtain when one of the ions is present in excess. It has been put forward as a working hypo-

thesis that, in a mixture of two strong electrolytes, each is ionised to the same degree as it would be if present alone in a solution having the same total ion concentration as the mixture. Arrhenius, for instance (*Zeitsch. physikal. Chem.*, 1888, **2**, 285; 1899, **31**, 218), used it in connexion with "neutral salt action," although it is often at variance with the requirements of the law of mass action; and Bray and Hunt, more recently (*J. Amer. Chem. Soc.*, 1911, **33**, 781), have found it to hold with considerable accuracy in the case of sodium chloride and hydrochloric acid mixtures.

When the values of the Ostwald function $\alpha^2/(1-\alpha)v$ were worked out for hypophosphorous acid, they were found to decrease arithmetically as the dilution v increased geometrically (over the range $v=8$ to $v=2048$). This connexion was expressed by the empirical formula

$$\alpha^2/(1-\alpha)v = 0{\cdot}1015 - \tfrac{1}{3\cdot5}\log v.$$

(All logarithms in this communication are to the base 10.)

In table I are shown under the various columns:

v = dilution.

λ = molecular conductivity.

α = degree of dissociation.

K_0 = the value of the Ostwald expression.

K_E = the value of the above empirical expression.

K = the value of $\alpha^2/(1-\alpha)v + \frac{1}{3\cdot5}\log v$, which is practically a constant.

[H$^+$] = the concentration of the hydrogen ions in the equilibria.

I = the total ionic concentration.

K_r = the value of van't Hoff's equation $\alpha^{1\cdot5}/(1-\alpha)\sqrt{v} = K_r$.

TABLE I.

v.	λ.	α.	K_0.	K_E.	K.	[H$^+$].	I.	K_r.
1	—	—	—	0·1015	—	—	—	—
2	140	0·360	0·1012	0·0929	—	0·1800	0·360	0·238
4	172	0·442	0·0876	0·0843	—	0·1105	0·221	0·263
8	207	0·532	0·0757	0·0757	0·1015	0·0665	0·1330	0·293
16	245	0·630	0·0670	0·0671	0·1014	0·0394	0·0788	0·330
32	281	0·722	0·0587	0·0585	0·1017	0·02256	0·0451	0·391
64	312	0·802	0·0508	0·0499	0·1014	0·01255	0·0251	0·454
128	335	0·861	0·0417	0·0413	0·1019	0·00672	0·0134	—
256	352	0·905	0·0336	0·0327	0·1024	—	—	0·566
512	361	0·928	0·0234	0·0241	0·1008	—	—	—
1024	367	0·944	0·0154	0·0155	0·1014	—	—	—
2048	368·3	0·948	0·0082	0·0069	0·1028	—	—	—
∞	389							

Van't Hoff's expression obviously fails, and Rudolphi's is still less applicable. Concordant values cannot be obtained for the constant in Partington's equation. Kraus and Bray's expression $\alpha^2/(1-\alpha)v = K + D(\alpha/v)^m$, applies over the same range as K_E wh

$D=0{\cdot}217$ and $m=0{\cdot}10$, but this gives a negative value of $K=-0{\cdot}090$.

It was hoped that the value of α could be found mathematically from the known value of the total ion concentration, or, of course, from the hydrogen-ion concentration, which is one half of it. This hope has been partly fulfilled, but the formula cannot apply to solutions more concentrated than $v=8$, beyond which the empirical formula fails. Nevertheless, the value of α as found agrees with that demanded by the total ion hypothesis up to the highest concentrations studied, which are considerably beyond the limit mentioned above.

Obviously the empirical formula fails before $v=3600$, where it gives negative values.

The data on which the values of α in the table are based are Ostwald's conductivity measurements at 25°, but the molecular conductivity at infinite dilution is not given by him, and had to be obtained from a consideration of several values for the H_2PO_2' ion combined with the value 347 for the hydrogen ion, which is the value now generally adopted (Kendall, T., 1912, **101**, 1283).

The data selected as being most consistent were:

(*a*) Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 191), from the sodium salt, finds the value for H_2PO_2' at 25° to be 41·8.

(*b*) Bredig (*ibid.*) finds 105·3 for the barium salt, whence $H_2PO_2'=39{\cdot}5$.

(*c*) Arrhenius (*Zeitsch. physikal. Chem.*, 1889, **4**, 99), using old units, gives a value for hypophosphorous acid which by conversion becomes 389, and this is the value adopted.

Hypophosphorous acid is one of the few acids which show a maximum of equivalent conductivity with increasing temperature; it occurs at 55° for this acid. This has been investigated by Arrhenius (*loc. cit.*), who refers it to anomalous values for the heat of neutralisation, and, therefore, for the heat of ionisation, which is negative instead of positive, as is normally the case.

Although hypophosphorous acid is described in the literature as a weak acid (Arrhenius, *ibid.*, and Abegg's "Theory of Electrolytic Dissociation" in Ahrens' Sammlung), yet it appears to be a "strong" acid according to more recent convention, which regards as "intermediate" acids those having ionisation constants of 0·001 to 0·01.

Experimental.

The determinations of the velocity constants were carried out in a thermostat at 25±0·05°. The methyl acetate was freshly distilled and free from acid. The hypophosphorous acid was an old

stock of Kahlbaum's chemically pure acid, which showed only a trace of oxidation to phosphorous acid, so that its titre was almost identical with either methyl-orange or phenolphthalein as indicator, but as the latter indicates the second hydrogen ion of phosphorous acid, the titre with this indicator was used in all cases where differences were involved, and the actual strength of the solution was based on its titre with methyl-orange as indicator.

Baryta solutions, prepared by diluting a $N/4$-solution to one-half, one-fourth, or one-eighth of its strength, were used for titrations. Steamed and dried Jena-glass bottles of 500 c.c. capacity were employed. The required amount of water was run in by 100, 50, and 25 c.c. pipettes, and 10 c.c. were drawn out to allow for the subsequent addition of that volume of ester. The necessary volumes of $N/2$- or $N/8$-acids were added, and the volume before the addition of the ester was 390 c.c. in each case. The general procedure was as in routine methods. Thus all experiments were strictly comparative.

Several titrations were carried out between fifty and seventy minutes after mixing, and were then adjusted to that for sixty minutes by making use of the velocity found for the early stages; the mean of these was used as zero time. In the stronger acid solutions, the final value was attained in ten days, and was employed in the equation $kt = \log x_\alpha - \log (x_\alpha - x)$. This equation is only strictly applicable in the early stages of the reaction, since it fails to take into account the reverse reaction between alcohol and acid. The more accurate velocity equation is $dx/dt = k'(a-x) - k''x^2$, where a represents the whole amount of ester (which is of the order of 5 per cent. greater than x_α), and where k', like k, embodies the large and practically constant value of the molecular concentration of water. Hence, remembering that $k'(a-x_\alpha) = k''x_\alpha^2$, one obtains the integrated expression

$$k't\frac{2a-x_\alpha}{x_\alpha} = \log\frac{x(a-x_\alpha)+ax_\alpha}{a(x_\alpha-x)} = \log\left[\frac{x_\alpha}{x_\alpha-x} + \frac{x(a-x_\alpha)}{a(x_\alpha-x)}\right].$$

From this it can be shown that the measurements should not extend beyond the first third of the reaction, in order that the change in the ratio k/k' may not exceed one-third per cent., and thus be within the experimental error. Within the prescribed limits, k/k' is equal to 1·055, and the relative error caused by using the simpler formula may be ignored.

In tables IIA and IIB, under the heading k, are shown the constants obtained; they are in all cases the mean of several values agreeing usually within 1 per cent., so that the error in k does not exceed one-half per cent., and is generally much less.

In each case, a formula enclosed in square brackets indicates the molecular concentration of the molecule or ion in question.

α represents the degree of dissociation of the acid concerned in table IIA, and of the hypophosphorous acid in IIB.

α_s and K_s are the values of α and K in solutions of hypophosphorous acid alone which have the same hydrogen-ion (or total ion) concentration as the mixed solution to which they relate. Both were taken from curves plotted from the data in table I. K_s (found) is calculated from the experimental results by a formula which is developed later.

The values of $k \times 10^6/[H^+]$ in the case of hydrochloric acid are obviously affected by the undissociated molecules, which possess about double the catalytic activity of the hydrogen ions (Snethlage, *Zeitsch. Elektrochem.*, 1902, **18**, 539, and Dawson, T., 1913, **103**, 2139). Lundén (*Zeitsch. physikal. Chem.*, 1904, **49**, 189) puts the activity of the hydrogen ions of hydrochloric acid in ester-catalyses equal to $[H^+]\{1+0{\cdot}34[H^+]\}$, and application of this formula gives the more consistent values under its heading.

The undissociated hypophosphorous acid molecules have a much smaller effect, but may account for the high value for its strongest

TABLE IIA.

$[H_3PO_2]$	[HCl].	$k \times 10^6$.	α.	$[H^+]$.	$k \times 10^6/[H^+]$.	$k \times 10^6$ $[H^+]\{1+0{\cdot}34[H^+]\}$.	
—	0·125	350	0·914	0·1143	3060	2950	
—	0·0625	174	0·934	0·0584	2990	2920	Mean
—	0·03125	87·1	0·950	0·0297	2930	2910	2930
—	0·01563	44·5	0·963	0·01505	2960	2940	
0·125	—	199·0	0·532	0·0665	(2990)		
0·0625	—	115·0	0·630	0·0394	2920		
0·03125	—	66·0	0·722	0·02255	2925	Mean 2925	
0·01563	—	36·7	0·802	0·01225	2925		

TABLE IIB.

$[H_3PO_2]$.	[HCl].	$k \times 10^6$.	Due to H_3PO_2.	$[H_2PO_2']$.	$[H^+]$.	α (found).	α_s.	K_s (found).	K_s.
0·125	0·01563	228	183·5	0·0626	0·0776	0·501	0·503	0·0784	0·0790
0·125	0·03125	262	175·1	0·0598	0·0895	0·478	0·477	—	—
0·125	0·0625	337	163	0·0556	0·1150	0·445	0·436	—	—
0·125	0·125	490	140	0·0478	0·1625	0·382	0·377	—	—
0·0625	0·01563	151	106·5	0·03635	0·0514	0·582	0·580	0·0714	0·0710
0·0625	0·03125	187	99·9	0·0341	0·0638	0·546	0·541	0·0749	0·0750
0·0625	0·0625	266	92	0·0314	0·0898	0·502	0·476	—	—
0·0625	0·125	422	72	0·0246	0·1389	0·393	0·400	—	—
0·03125	0·01563	104	59·5	0·0203	0·03535	0·650	0·648	0·0654	0·0652
0·03125	0·03125	140·6	53·5	0·01825	0·0479	0·584	0·592	0·0700	0·0698
0·03125	0·0625	220	46·0	0·0157	0·0741	0·502	0·510	—	—
0·03125	0·125	389	39·0	0·0133	0·1276	0·426	0·416	—	—
0·01563	0·01563	76·6	32·1	0·01095	0·0260	0·701	0·698	0·0609	0·0608
0·01563	0·03125	117·0	29·9	0·01025	0·0400	0·656	0·626	0·0668	0·0672
0·01563	0·0625	200	26	0·00887	0·0673	0·568	0·528	0·0753	0·0762
0·01563	0·125	370	20	0·00683	0·1211	0·437	0·426	—	—

solution, where they constitute nearly half of the acid. As the acid does not give a definite affinity constant, the formula of Taylor (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, **2**, Nos. 34, 35, 37) cannot be applied to estimate this effect, but indicates that it is very small.

Discussion of Results.

In order to avoid the difficulty due to the uncertainty as to the effect of undissociated hydrochloric acid molecules, in each case the value for the appropriate concentration of hydrochloric acid (as shown in table IIA) is subtracted from the constant obtained, and the remainder is attributed to the hydrogen ions derived from the hypophosphorous acid. If this remainder is divided by 2930, the mean value of $k \times 10^6 \div [H^{\cdot}]$, one obtains the concentration of the corresponding hydrogen and H_2PO_2' ions. (The experimental error is considerably magnified by this subtraction, and especially so in those cases where the hydrochloric acid ions are considerably in excess of those of the hypophosphorous acid.) The total hydrogen-ion concentration is obtained by adding that due to the hydrochloric acid alone. One assumes implicitly that the ionisation of the hydrochloric acid is not depressed, and, although this cannot be rigidly true, a comparison of the ionisation values of the two acids shows that the effect on the stronger acid would be negligible compared with that on the weaker acid. Moreover, as the molecules of the hydrochloric acid possess a catalytic activity, the total activity of the hydrochloric acid would be slightly increased, and so tend to lead to slightly high values for α.

The values for the ionisation of hydrochloric acid were selected from a mass of discordant data which vary by 3 per cent. or more in the literature on the subject, but the recent careful determinations by Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781) were used, by interpolation, as they agree well with the means of all others and also with those of Goodwin and Haskell (*Physical Rev.*, 1904, **19**, 369), which, however, were carried out at 18°.

It is clearly seen that α for hypophosphorous acid in any mixture approximates closely to α_s, the degree of ionisation it would have if present alone in the same concentration of hydrogen ions.

If we consider one mole of hypophosphorous acid in v litres of water, which also contain h equivalents of extraneous hydrogen ions, we have $\frac{\alpha(\alpha+h)}{(1-\alpha)v} = K_1$, and, considering a solution of one mole alone at a dilution v_1, such that the concentration of hydrogen ions is the same as in the first solution, α_1 being its degree

of ionisation, we have $\frac{\alpha_1^2}{(1-\alpha_1)v_1} = 0{\cdot}1015 - \frac{1}{3\cdot5}\log v_1 = K_2$, but $\alpha_1 = \alpha$, as already found, and, since the hydrogen-ion concentrations are equal, $\frac{a+h}{v} = \frac{a_1}{v_1}$. Therefore $v_1 = v\frac{a}{a+h}$ and

$$K_1 = \frac{a(a+h)}{(1-a)v} = \frac{\alpha_1^2}{(1-\alpha_1)v_1} = K_2 =$$

$$0{\cdot}1015 - \tfrac{1}{3\cdot5}\log\frac{va}{a+h} = 0{\cdot}1015 - \tfrac{1}{3\cdot5}\log\frac{a}{[\mathrm{H}^\cdot]}.$$

This formula enables us to derive from the experimentally determined α a value of K_2 which is seen to agree well with that found from a graph for a hypophosphorous acid solution having the same hydrogen-ion concentration, when this does not exceed that of a $N/8$-solution (that is, 0·0665).

K_1 is not shown, as it is very susceptible to experimental error.

Attempts have been made, so far unsuccessfully (except possibly for phosphorous acid), to apply an analogous formula to other fairly strong acids, and also to seek for a theoretical significance.

Conclusions.

1. The hypothesis that, in a mixture of two electrolytes, each is ionised to the same extent as it would be if present alone in a solution having the same concentration of ions, has been found to apply to hypophosphorous acid in presence of hydrochloric acid.

2. The empirical formula $\alpha^2/(1-\alpha)v = 0{\cdot}1015 - \frac{1}{3\cdot5}\log_{10}v$ holds for hypophosphorous acid in dilutions down to $v = 8$.

3. In virtue of these two facts, the ionisation equilibria of hypophosphorous acid in the presence of extraneous hydrogen ions is represented in dilute solutions by

$$[\mathrm{H}^\cdot][\mathrm{H_2PO_2'}]/[\mathrm{H_3PO_2}] = 0{\cdot}1015 - \tfrac{1}{3\cdot5}\log_{10}\alpha/[\mathrm{H}^\cdot].$$

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CVI.—*Derivatives of Gallic Acid. Part I.* Synthesis of 4-Hydroxy-3 : 5-dimethoxyphthalic Acid.*

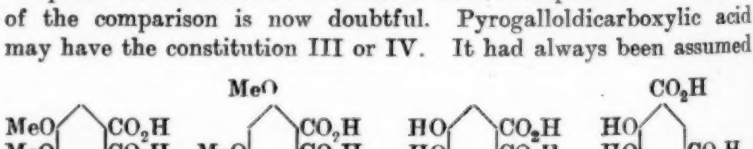
By Rupchand Lilaram Alimchandani and Andrew Norman Meldrum.

Hydroxy- and methoxy-phthalic acids are often obtained as degradation products of naturally occurring substances, such as dyes and alkaloids. Windaus, for instance, studied the alkaloids colchiceine, which contains three methoxy-groups and a hydroxy-group, and colchicine, which contains four methoxy-groups; by oxidising colchicine, which he regards as the methyl ether of colchiceine, he obtained a trimethoxyphthalic acid (*Sitzungsber. Heidelberger Akad. Wiss.*, 1910, 1; 1914, Abh. 18). Feist had previously studied columbamine, which contains four methoxy-groups and a hydroxy-group. By methylating columbamine, he obtained the methyl ether of columbamine, which on oxidation gave a trimethoxyphthalic acid (*Arch. Pharm.*, 1907, **245**, 586). Recently, Feist and Sandstede have again studied this derivative (*Arch. Pharm.*, 1918, **256**, 1). The following table shows the melting points observed for the substances:

	Acid.	Anhydride.
Windaus	175—176°	143—144°
Feist	200°	—
Feist and Sandstede	185°	128°

Feist and Sandstede, in spite of the differences in melting point, conclude that their trimethoxyphthalic acid is identical with that obtained by Windaus from colchicine.

There are two possible trimethoxyphthalic acids, I and II, and, obviously, synthetic work on these acids is valuable. Feist converted pyrogalloldicarboxylic acid into its trimethyl ether, and on comparison found it to be different from his compound. The value of the comparison is now doubtful. Pyrogalloldicarboxylic acid may have the constitution III or IV. It had always been assumed

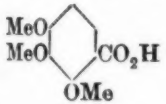


* A preliminary note on the subject of this paper was read at the Indian Science Congress, in the Chemistry Section, January, 1919.

to be III, in view of the fact that it had been synthesised from gallic acid; recently, Hemmelmayr (*Monatsh.*, 1917, **38**, 77) obtained it, using gallic acid and potassium hydrogen carbonate, in almost theoretical yield. Voswinckel and de Weerth had already suggested that in this synthesis migration of the carboxyl group of gallic acid must occur; the resulting acid does not give an anhydride, and they concluded that it has the constitution IV (*Ber.*, 1912, **45**, 1242).

The authors undertook the synthesis of 3:4:5-trimethoxyphthalic acid (I) by a method which should leave no doubt as to the constitution of the product. After this had been accomplished, they learnt that Bargellini and Molina had carried out the same synthesis, and by the same method (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 146). There is, however, a considerable difference in the details, since the authors obtained derivatives of syringic acid (VI), whilst Bargellini and Molina did not. These derivatives of syringic acid are important in connexion with columbamine, and perhaps with colchiceine, both of which alkaloids conceivably contain a syringic acid residue. By methylation, the authors were able to obtain a trimethoxyphthalic acid (I) which is identical with Bargellini and Molina's acid.

The constitution I and VII for the respective phthalic acids can be regarded as established in view of (1) the synthetic method employed, (2) the fact that the acids give anhydrides, (3) the fact that the acids can be reconverted into the substances V and VI, respectively, from which they were synthesised.



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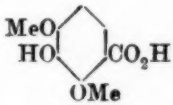

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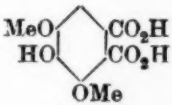


(VII.)

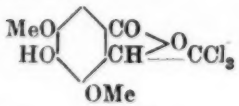
The two substances I and VII are genuine derivatives of gallic acid. Compound I (m. p. 176—177°) is different from the trimethyl ether of pyrogalloldicarboxylic acid (Feist, m. p. 195°), which therefore is not a true gallic acid derivative. Pyrogalloldicarboxylic acid is therefore IV, and when this acid is synthesised from gallic acid, the carboxyl group of gallic acid must be displaced, as Voswinckel and de Weerth suggested.

The method employed, which is due to Fritsch, consists in the condensation of a hydroxybenzoic acid with chloral, leading to the formation of a trichloromethylphthalide; the trichloromethyl group is eliminated, and the resulting phthalide is oxidised to a dicarboxylic acid, which can be only an ortho-phthalic acid (*Annalen*, 1897, **296**, 358; 1898, **301**, 360; see also T., 1911, **99**, 1712).

Fritsch recommends that in carrying out the condensation with chloral, the hydroxybenzoic acid should be used in the form of its methoxy-ester. This is not always necessary, for the authors find that the trimethyl ether of gallic acid and even gallic acid undergo the condensation, yielding trichloromethylphthalides.

3:4:5-Trimethoxybenzoic acid (V) and chloral give a substance which has not the composition that was at first expected. On investigation, it was found that the sulphuric acid employed as the condensing agent hydrolyses the trimethoxybenzoic acid and produces syringic acid (VI). The original method of obtaining syringic acid from trimethoxybenzoic acid was to hydrolyse by means of hydrobromic acid (Graebe and Martz, *Annalen*, 1905, **340**, 220). Bogert and Isham (*J. Amer. Chem. Soc.*, 1914, **36**, 519) introduced the use of fuming sulphuric acid. For some time the authors were in doubt as to the acid they obtain, using ordinary sulphuric acid, for it has not the aromatic odour which Bogert and Isham ascribe to syringic acid. The authors therefore satisfied themselves that the substance is syringic acid by preparing its methyl ester, the acetyl derivative of the methyl ester, and, by oxidation, 3:5-dimethoxy-*p*-benzoquinone. Hence the use of ordinary sulphuric acid in making syringic acid has the advantage of not giving rise to the impurity, possessing an aromatic odour, which Bogert and Isham obtained.

Whether trimethoxybenzoic acid, or its methyl ester, or syringic acid is condensed with chloral, the product is the same, namely, 4-hydroxy-3:5-dimethoxy-2-trichloromethylphthalide (VIII). Syringic acid gives the larger and purer yield. In place of VIII, Bargellini and Molina obtained the corresponding trimethoxy-compound; they carried out the reaction using trimethoxybenzoic acid methyl ester. So far as the authors can judge, the difference does not depend on the use of the ester; it is probably due to a difference in the sulphuric acid employed, or to the higher temperature at which the reaction was carried out in India, or to both these causes.



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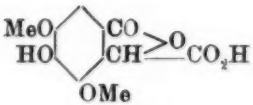

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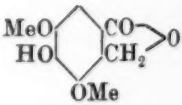

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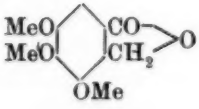

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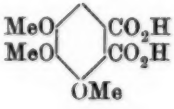
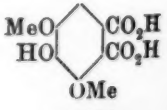


(I.)



(VII.)

The trichloromethylphthalide, on hydrolysis, gives 4-hydroxy-3:5-dimethoxyphthalide-2-carboxylic acid (IX). This, when heated, loses carbon dioxide and gives 4-hydroxy-3:5-dimethoxyphthalide (X). From this, on methylation, 3:4:5-trimethoxyphthalide (XI) is obtained, and this, on oxidation, gives rise to 3:4:5-trimethoxyphthalic acid (I), which readily gives an anhydride. When this anhydride is dissolved in sulphuric acid and the solution is poured into water, the product is 4-hydroxy-3:5-dimethoxyphthalic acid (VII), which also readily gives an anhydride. This acid is the oxidation product of the phthalide (X), from which, however, the authors were unable to obtain it by direct oxidation. Boiling with hydrochloric acid converts I into V and VII into VI.

Experimental.

Salts of 3:4:5-*Trimethoxybenzoic Acid.*

Trimethoxybenzoic acid was prepared according to Graebe and Martz's method (*loc. cit.*). The following hitherto undescribed salts were prepared and analysed.

Sodium Salt.—The acid was dissolved in sodium hydroxide solution, and a hot concentrated solution of the alkali was added. The sodium salt gradually crystallised in long, rectangular plates; it was collected, washed quickly with water, crushed on a porous tile, and dried in a desiccator (Found: Na = 9·84. $C_{10}H_{11}O_5Na$ requires Na = 9·83 per cent.).

Potassium Salt.—This was obtained in the same manner as the sodium salt. It crystallises in plates (Found: K = 15·97. $C_{10}H_{11}O_5K$ requires K = 15·60 per cent.).

Lead Salt.—The acid was dissolved in very dilute ammonia, the excess of ammonia evaporated, and a dilute solution of neutral lead acetate was added. The lead salt crystallises in silky needles [Found: Pb = 32·52. $(C_{10}H_{11}O_5)_2Pb$ requires Pb = 32·91 per cent.].

Syringic Acid (VI).

3:4:5-Trimethoxybenzoic acid (25 grams) was dissolved in sulphuric acid (100 c.c. of 96—98 per cent.), and, after about twenty-four hours, the liquid was poured into water (200 c.c.), when syringic acid was precipitated in silky needles (19 grams). It sinters at 204° and melts at 206—207°.

Small amounts were converted into methyl syringate (hydrated: m. p. 84—86°), methyl acetylsyringate (m. p. 131°), and 3:5-dimethoxy-*p*-benzoquinone (m. p. 255°).

4-Hydroxy-3:5-dimethoxy-2-trichloromethylphthalide (VIII).

Syringic acid (7 grams), chloral hydrate (9 grams), and sulphuric acid (50 c.c.) were mixed together, and, on vigorous shaking, the solids dissolved. After about forty-eight hours, the liquid was poured on ice. A white solid separated, which was collected and washed with water, the yield being 10 grams. The substance crystallises from methyl alcohol in truncated, rectangular plates melting at 172—173° (Found: Cl = 32·50. $C_{11}H_9O_5Cl_3$ requires Cl = 32·50 per cent.).

The *acetyl* derivative of the above compound was prepared, using acetic anhydride and a few drops of concentrated sulphuric acid. It crystallises from absolute alcohol in small clusters of prisms melting at 139° (Found: Cl = 28·78. $C_{13}H_{11}O_6Cl_3$ requires Cl = 28·80 per cent.).

Sodium Compound.—It was possible to prepare the sodium derivative of the above trichloro-compound without hydrolysing it. The substance was dissolved in ice-cold dilute sodium hydroxide solution, and concentrated sodium hydroxide solution (ice-cold) was added. A yellow *sodium* compound separated, which was rapidly collected, dried on porous tile, and then analysed (Found: Na = 7·08. Calc.: Na = 6·6 per cent.).

4-Hydroxy-3:5-dimethoxyphthalide-2-carboxylic Acid (IX).

The trichloro-compound (15 grams) was boiled with a solution of sodium hydroxide (15 grams) in water (125 c.c.). The substance first turned yellow, then gradually dissolved, and the solution became dark. On acidifying this solution, the free acid was obtained in white needles (11 grams). For analysis, it was crystallised from acetic acid, and finally from water.

The substance contains water of crystallisation; it was found to effloresce at the ordinary temperature and to lose water completely at 100—110°. It then melts and decomposes at 187° (Found: H_2O = 6·47. $C_{11}H_{10}O_7,H_2O$ requires H_2O = 6·62 per cent.).

The anhydrous substance was analysed (Found: C = 52·16; H = 4·23. $C_{11}H_{10}O_7$ requires C = 52·00; H = 3·94 per cent.).

The *calcium* salt crystallises with one molecule of water. When heated, it decomposes, for concordant figures for the water of crystallisation could not be obtained [Found: Ca = 6·98. $(C_{11}H_9O_7)_2Ca,H_2O$ requires Ca = 7·08 per cent.].

The acid, on titration with standard alkali, gave no definite result, as there was no sharp neutralisation point.

4-Hydroxy-3:5-dimethoxyphthalide (X).

The phthalidecarboxylic acid (14 grams), along with naphthalene (40 grams), was heated to 200—210°, until the evolution of carbon dioxide ceased. Naphthalene was then removed in a current of steam, and the solution of the phthalide in water was filtered. It crystallises in prismatic needles melting at 144°. For analysis, it was recrystallised from ethyl acetate (Found: C=57·19; H=4·97. $C_{10}H_{10}O_5$ requires C=57·15; H=4·76 per cent.).

Oxidation of this substance did not give a definite product.

3:4:5-Trimethoxyphthalide (XI).

The phthalide just described (5 grams) was dissolved in sodium hydroxide (15 grams) dissolved in water (100 c.c.). To this, dimethyl sulphate (20 c.c.) was added in small amounts, and the mixture was heated. On acidification, needle-shaped crystals were obtained, which were recrystallised from ethyl acetate for analysis. The substance melts at 135—136° (Bargellini and Molina give 134—135°) (Found: C = 59·1; H = 5·64. Calc.: C = 58·94; H=5·36 per cent.).

3:4:5-Trimethoxyphthalic Acid (I).

3:4:5-Trimethoxyphthalide (8 grams) was dissolved in excess of dilute potassium hydroxide, and to the cold solution potassium permanganate (8 grams) dissolved in water (260 c.c.) was added. After about forty-eight hours, the manganese dioxide was filtered off, and the bluish-green colour of the filtrate was removed by means of sulphurous acid. The solution was then evaporated to small bulk, filtered, and acidified, when 3:4:5-trimethoxyphthalic acid crystallised in white, rhombic plates. For analysis, it was recrystallised from water, when it melted and decomposed at 176—177° (Bargellini and Molina give 174°) (Found: C=51·46; H=4·84. Calc.: C=51·56; H=4·70 per cent. Equivalent found: 128·3. Calc.: 128).

3:4:5-Trimethoxyphthalic Anhydride.

The anhydride was prepared by heating the phthalic acid carefully at its melting point. The product crystallises from benzene in clusters of needles melting at 147° (Bargellini and Molina give 143°). (Equivalent found: 118·8. Calc.: 119.)

A mixture of the trimethoxyphthalic acid with concentrated

hydrochloric acid was boiled under reflux for an hour. On cooling, crystals of trimethoxybenzoic acid (V) were obtained.

4-Hydroxy-3:5-dimethoxyphthalic Acid (VII).

3:4:5-Trimethoxyphthalic anhydride (4 grams) and sulphuric acid (20 c.c. of 96—98 per cent.) were mixed, when the anhydride dissolved easily. After three days, the solution was poured on ice, when a crystalline substance separated. On recrystallisation from water, it melted and decomposed at 225—227° (Found: C=49·35; H=4·21. $C_{10}H_{10}O_7$ requires C=49·58; H=4·13 per cent.).

The results of titration with standard alkali were untrustworthy, as there was no sharp neutralisation point.

4-Hydroxy-3:5-dimethoxyphthalic Anhydride.

The anhydride was obtained by heating the phthalic acid just described at its melting point. The product crystallises from toluene in needles melting at 177—179° (Found: C=53·6; H=3·9. $C_{10}H_8O_6$ requires C=53·6; H=3·6 per cent.).

Syringic Acid from 4-Hydroxy-3:5-dimethoxyphthalic Acid.

A mixture of the phthalic acid (0·5 gram) and concentrated hydrochloric acid (20 c.c.) was boiled under reflux for about four hours. The hot solution was filtered, and white, silky needles separated from the filtrate. The substance was recrystallised, and was found to be syringic acid (VI).

A study of the various substances formed by the interaction of chloral and gallic acid is almost concluded.

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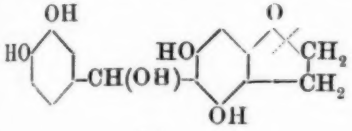
AHMEDABAD, INDIA. [*Received, October 24th*, 1919.]

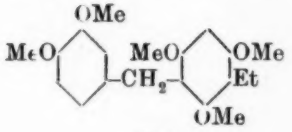
CVII.—*The Constitution of Catechin.* Part I.*

By MAXIMILIAN NIERENSTEIN.

KOSTANECKI and Lampe (*Ber.*, 1907, **40**, 720) have shown that when catechin tetramethyl ether is reduced with metallic sodium and alcohol, an oil (desoxyhydrocatechin tetramethyl ether) is formed, which on further methylation yields a crystalline pentamethyl derivative, and they regarded this as 2:4:6:3′:4′-pentamethoxy-3-ethyldiphenylmethane (II). Its production was con-



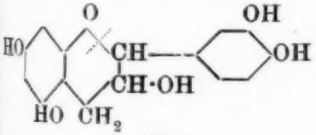
(I.)



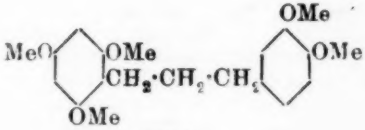
(II.)

sidered by them as being strong evidence in favour of their coumaran formula for catechin (I), especially as Alexander (*Ber.*, 1892, **25**, 2409) had previously found that coumaran itself may be reduced under the same conditions to *o*-ethylphenol:

Ryan and Walsh (*Sci. Proc. Roy. Dublin Soc.*, 1916, **15**, 113) have pointed out that these deductions are in no way conclusive, since the reactions described by Kostanecki and Lampe can also be explained on the basis of the original chroman formula (III) proposed by A. G. Perkin and Yoshitake (T., 1902, **81**, 1172). Ryan and Walsh have consequently suggested formula IV as an alternative to Kostanecki and Lampe's formula (II) for the methylated reduction product.



(III.)

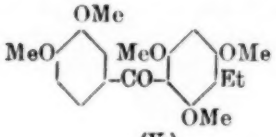


(IV.)

With the view of deciding between the chroman and coumaran

* For a complete summary of the literature see Perkin and Everest, *The Natural Organic Colouring Matters*, 1918.

formula,* Ryan and Walsh attempted the synthesis of 2 : 4 : 6 : 3′ : 4′-pentamethoxy-3-ethyldiphenylmethane (II), but owing to the lack of material they were unable to accomplish it. Both this substance and 3:4:2′:4′:6′-*pentamethoxy-αγ-diphenylpropane* (IV) have now been synthesised according to the following schemes: 2 : 4 : 6 : 3′ : 4′-pentamethoxy-3-ethylbenzophenone (V) was reduced to 2:4:6:3′:4′-*pentamethoxy-3-ethyldiphenylcarbinol* (VI), which on further reduction gave 2:4:6:3′:4′-*pentamethoxy-3-ethyldiphenylmethane* (II). 2:4:6-Trimethoxyphenyl



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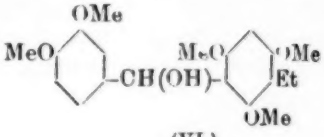
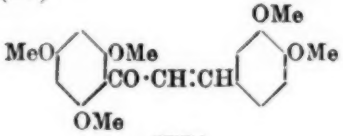
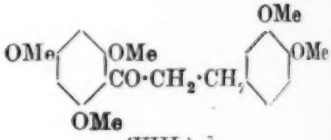


(VI.)

3:4-dimethoxystyryl ketone (VII) was first reduced to 2:4:6-*trimethoxyphenyl* 3:4-*dimethoxy-β-phenylethyl ketone* (VIII), and subsequently to 3:4:2′:4′:6′-*pentamethoxy-αγ-diphenylpropane* (IV).



(VII.)



(VIII.)

As will be seen from the following summary of the melting points and mixed melting points of these substances, neither 2 : 4 : 6 : 3′ : 4′-pentamethoxy-3-ethyldiphenylmethane (II) nor 3:4:2′:4′:6′-pentamethoxy-αγ-diphenylpropane (IV) is identical with the methylated reduction product described by Kostanecki and Lampe:

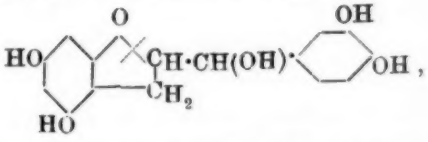
Melting point of Kostanecki and Lampe's product, 83—84°.

Melting point of 2:4:6:3′:4′-pentamethoxy-3-ethyldiphenylmethane (II), 91—92°.

Mixed m. p. with Kostanecki and Lampe's product, 49—65°.

Melting point of 3:4:2′:4′:6′-pentamethoxy-αγ-diphenylpropane (IV), 87—88°.

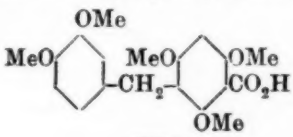
* It should be noted that the coumaran formula:



which has also been considered by Kostanecki and Lampe (*loc. cit.*) would also lead to 3:4:2′:4′:6′-pentamethoxy-αγ-diphenylpropane (IV.).

Mixed m. p. with Kostanecki and Lampe's product, 61—69°.

During the course of the present investigation, it was found that Kostanecki and Lampe's methylated reduction product, which has the empirical formula* $C_{20}H_{26}O_5$, yields on oxidation the acid, $C_{19}H_{22}O_7$, which melts at 150—151°. As may be seen, this oxidation is accompanied by the loss of one carbon atom, and this was found to be a general reaction in the case of compounds,† $R{\cdot}CH_2{\cdot}CH_3$, which yield the corresponding acids, $R{\cdot}CO_2H$. Similarly, 2:4:6:3′:4′-pentamethoxy-3-ethyldiphenylmethane (II) gives 2:4:6:3′:4′-*pentamethoxydiphenylmethane*-3-*carboxylic acid*,



(IX.)

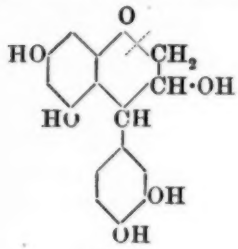
(IX), which melts at 108°. 3:4:2′:4′:6′-Pentamethoxy-αγ-diphenylpropane (IV), on the other hand, is recovered unchanged, which still further accentuates the differences between Kostanecki and Lampe's methylated reduction product and 2:4:6:3′:4′-pentamethoxy-3-ethyldiphenylmethane (II) and 3:4:2′:4′:6′-pentamethoxy-αγ-diphenylpropane (IV).

These observations indicate that on reduction and subsequent methylation, the coumaran or the chroman nucleus yields the product, $C_{18}H_{21}O_5{\cdot}CH_2{\cdot}CH_3$, from which, on oxidation, the acid, $C_{18}H_{21}O_5{\cdot}CO_2H$, is produced. The only coumaran formula in agreement with these facts is that proposed by Kostanecki and Lampe (I), but, as previously pointed out, this formula is untenable. By a slight modification of Perkin and Yoshitake's chroman formula (III), the observations recorded in this paper become, however, readily explicable. Thus, considering catechin to be represented by formula X, Kostanecki and Lampe's methyl-

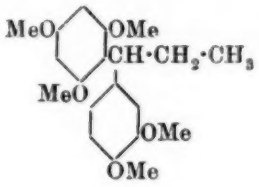
* The empirical formula given by Kostanecki and Lampe (*Ber.*, 1907, **40**, 722) is $C_{20}H_{26}O_6$, which requires C=66·3; H=7·2 per cent. They calculate and find, however, correctly for $C_{20}H_{26}O_5$ (Found: C=69·36; H=7·51. Calc.: C=69·29; H=7·59 per cent.). I have also analysed this substance and find C=69·1; H=7·6 per cent. as required by $C_{20}H_{26}O_5$.

† The products used were: 2:4-dimethoxyethylbenzene, 2:4-dihydroxyethylbenzene and 2:3:4-trihydroxyethylbenzene. They were prepared from the corresponding ketones (compare Clemmensen, *Ber.*, 1913, **46**, 1837; 1914, **47**, 51, 681). Of these substances 2:4-*dimethoxyethylbenzene* has so far not been described. It is an oil boiling at 238–241°/767 mm. (Found: C=72·0; H=8·6.—$C_{10}H_{14}O_2$ requires C=72·3; H=8·4 per cent.). The acids obtained on oxidation: dimethyl-β-resorcylic, β-resorcylic and pyrogallolcarboxylic acid respectively, had the correct melting points. Mixed melting points showed no depression.

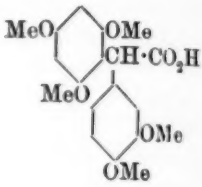
ated reduction product becomes 3:4:2′:4′:6′-pentamethoxy-αα-diphenylpropane (XI), and the acid obtained from it 3:4:2′:4′:6′.



(X.)



(XI.)



(XII.)

pentamethoxydiphenylacetic acid (XII). This acid (XII) has been prepared by the Grignard reaction from carbon dioxide and 3:4:2′:4′:6′-*pentamethoxydiphenylmethyl chloride*, and was found to be identical in every respect with the acid obtained by the oxidation of Kostanecki and Lampe's methylated reduction product.

Experimental.

2:4:6:3′:4′-*Pentamethoxy*-3-*ethyldiphenylmethane* (II).

The 2:4:6:3′:4′-pentamethoxy-3-ethylbenzophenone (V) required for the reduction was prepared by Ryan and Walsh's method (*loc. cit.*). It crystallised from dilute alcohol in needles melting at 127—129°, whereas Ryan and Walsh give 123—124° (Found: C = 66·5; H = 6·9. Calc.: C = 66·7; H = 6·7 per cent.).

2:4:6:3′:4′-*Pentamethoxy*-3-*ethyldiphenylcarbinol* (VI).

A solution of 5 grams of the ketone in 70 c.c. of alcohol is heated for nineteen hours on a water-bath with an aqueous solution of 15 grams of potassium hydroxide and 25 grams of zinc dust. The solution is filtered while hot, and the zinc dust extracted several times with alcohol. The filtrate is concentrated to about 20 c.c., and 170 c.c. of water are added. The precipitate crystallises from dilute alcohol in needles, which melt at 112°. The carbinol is soluble in the usual organic solvents, with the exception of light petroleum. With concentrated sulphuric acid, it yields a deep red solution (Found *: C = 66·1; H = 7·3 $C_{20}H_{26}O_6$ requires C = 66·3; H = 7·2 per cent.).

By digesting with acetic anhydride and anhydrous sodium acetate, the *acetyl* derivative is easily prepared. It crystallises from alcohol in small cubes, which melt at 109—110°. Since the

* Dried over phosphoric oxide in a vacuum.

melting points of the carbinol and that of the acetyl derivative are practically identical, it is to be noted that mixtures melted 12—17° below the melting points of the compounds (Found *: C = 65·4; H = 7·2. $C_{22}H_{28}O_7$ requires C = 65·3; H = 6·9 per cent.).

The *methyl* derivative is prepared by the action of methyl sulphate and alkali on an alcoholic solution of the carbinol. It crystallises from methyl alcohol in prismatic needles, which melt at 94°. Diazomethane does not methylate this carbinol (compare Geake and Nierenstein, T., 1915, **107**, 1491; Dean and Nierenstein, T., 1916, **109**, 596) (Found *: C = 66·7; H = 7·7. $C_{21}H_{28}O_6$ requires C = 67·0; H = 7·4 per cent.).

2:4:6:3′:4′-*Pentamethoxy*-3-*ethyldiphenylmethane* (II).

Three grams of the carbinol dissolved in 100 c.c. of alcohol are reduced with 12 grams of metallic sodium. The solution is heated on a water-bath for twelve hours, when all the sodium disappears. After removal of the alcohol with steam, and cooling, a resinous mass is deposited, the alcoholic solution of which leaves, on evaporation, an oil, which becomes semi-solid on keeping over phosphoric oxide. This product is again dissolved in a little alcohol and precipitated with water, and this process of purification is repeated until a dry specimen dissolves in concentrated sulphuric acid without any coloration. It crystallises from a mixture of benzene and alcohol (2:1) in small, prismatic needles, which melt at 91—92°. The substance is soluble in the usual organic solvents, with the exception of light petroleum. The alcoholic solution shows a pale blue fluorescence. The average yield is 64 per cent. of the theoretical. Two different preparations were used for analysis (Found †: C = 69·5, 69·1; H = 7·9, 8·1. $C_{20}H_{26}O_5$ requires C = 69·3; H = 7·5 per cent.).

2:4:6:3′:4′-*Pentamethoxydiphenylmethane*-3-*carboxylic Acid* (IX).

To a suspension of 1·4 grams of the diphenylmethane derivative (II) in 50 c.c. of 2*N*-potassium hydroxide, 50 c.c. of 2*N*-potassium permanganate are added, and the solution is heated on a water-bath for five and a-half hours. The cold solution is filtered, acidified with dilute sulphuric acid, and extracted several times with ether. The dried ethereal extract leaves a residue, which crystallises from water in silky needles melting at 108°, carbon

* Dried over phosphoric oxide in a vacuum.

† Dried over paraffin in a vacuum.

dioxide being evolved. The yield is 0·6 gram (Found*: C=62·9; H=6·3. $C_{19}H_{22}O_7$ requires C=63·0; H=6·1 per cent.).

A solution of 0·46 gram of the acid in dry ether gives, on treatment with an ethereal solution of diazomethane (from 7 c.c. of nitrosomethylurethane), a quantitative yield of the *methyl* ester. It crystallises from benzene in prismatic needles melting at 81°, carbon dioxide being evolved. On warming with dilute alkali, the original acid is regenerated (Found†: C=63·5; H=6·3. $C_{20}H_{24}O_7$ requires C=63·8; H=6·4 per cent.).

3:4:2′:4′:6′-*Pentamethoxy*-αγ-*diphenylpropane* (IV).

Tutin and Caton (T., 1910, **97**, 2067) have prepared the 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone (VII) required for the reduction by the action of finely divided sodium on an ethereal solution of veratraldehyde and trimethoxyacetophenone. Both this method and that described by Göschke and Tambor (*Ber.*, 1912, **45**, 186) for the preparation of similar substances were tried, with the result that the following method was finally adopted. To a warm alcoholic solution of 3 grams of veratraldehyde and 3·8 grams of trimethoxyacetophenone, 10 grams of a 50 per cent. solution of alcoholic potassium hydroxide are slowly added. The mixture is allowed to remain for forty-eight hours, diluted with water, and the alcohol removed by distillation with steam. On cooling, a viscous mass is formed, which is washed several times with water, and subsequently dissolved in alcohol and precipitated with water. It crystallises from dilute alcohol in yellow, prismatic needles, which melt at 84—85°; after remaining over paraffin in a vacuum for some time, the melting point rises to 117—118°. These two melting points are in agreement with those given by Tutin and Caton, who find 85° for the product containing one molecule of alcohol and 117·5° for the alcohol-free product.

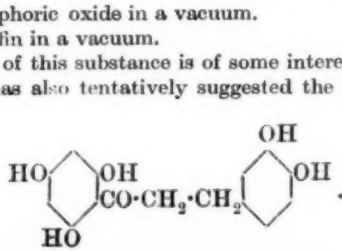
2:4:6-*Trimethoxyphenyl* 3:4-*Dimethoxy*-β-*phenylethyl Ketone*‡ (VIII).

Bargellini's method (*Gazzetta*, 1911, **41**, ii, 442; 1912, **42**, ii, 425) for the reduction of methoxyphenyl styryl ketones was

* Dried over phosphoric oxide in a vacuum.

† Dried over paraffin in a vacuum.

‡ The preparation of this substance is of some interest, since A. G. Perkin (T., 1905, **87**, 405) has also tentatively suggested the following formula for catechin:



found to give a colourless product, whereas the reduction with acetic acid and zinc dust gives a slightly coloured substance. The former process may be conveniently carried out in the apparatus devised by Ellis and Gardner (*Biochem. J.*, 1918, **12**, 72) for the reduction of cholesterol. The product crystallises from alcohol in needles, which melt at 91°, the average yield being 92 per cent. of the theoretical. It is soluble in the usual organic solvents. The alcoholic solution is turned faintly pink by the addition of ferric chloride (Found*: C = 66·8, 66·4; H = 7·2, 6·9. $C_{20}H_{24}O_6$ requires C = 66·7; H = 6·7 per cent.).

3:4:2′:4′:6′-Pentamethoxy-αγ-diphenylpropane (IV).

Three grams of 2:4:6-trimethoxyphenyl 3:4-dimethoxy-β-phenylethyl ketone dissolved in 100 c.c. of alcohol are heated for six hours with 15 grams of metallic sodium. The greater part of the alcohol is removed by evaporation, and the alcoholic solution diluted with water. The precipitate which separates crystallises from dilute alcohol in small needles melting at 87—88°. The average yield is 74 per cent. of the theoretical (Found: C = 69·5, 69·2; H = lost, 7·8. $C_{20}H_{26}O_5$ requires C† = 69·3; H = 7·5 per cent.).

Oxidation of Kostanecki and Lampe's Methylated Reduction Product to 3:4:2′:4′:6′-Pentamethoxydiphenylacetic Acid (XII).

Twelve grams of Kostanecki and Lampe's product suspended in 300 c.c. of a 20 per cent. solution of potassium hydroxide in water are oxidised on a boiling-water bath for four hours with 12 grams of potassium permanganate dissolved in 200 c.c. of water. The solution is filtered while hot, and, after cooling, is acidified with dilute sulphuric acid. The dark-coloured precipitate thus obtained is crystallised several times from water, animal charcoal being

In this case 2:4:6-trimethoxyphenyl 3:4-dimethoxy-β-phenylethyl ketone (VIII), which melts at 91°, should be identical with catechin pentamethyl ether. The latter substance has been prepared by Kostanecki and Lampe by the action of methyl sulphate (*Ber.*, 1906, **39**, 4011). They give its melting point as 95°. The author (*Annalen*, 1913, **396**, 197), who has obtained this substance by the action of diazomethane, finds its melting point to be 84–86°. Catechin pentamethyl ether was therefore also prepared according to Kostanecki and Lampe's method, and was found to melt at 84–86°. (Found: C = 66·3; H = 6·9. Calc.: C = 66·5; H = 6·8 per cent.). This suggests that the melting point given by Kostanecki and Lampe is a clerical error. The melting points of mixtures of catechin pentamethyl ether and 2:4:6-trimethoxyphenyl 3:4-dimethoxy-β-phenylethyl ketone showed depressions of 18–21°, thus proving that these two substances are not identical, which consequently excludes the above formula for catechin.

* Dried over phosphoric oxide in a vacuum. † Dried at 110°.

used, when long, hairy, colourless needles are obtained, which melt at 150—151°, carbon dioxide being evolved. The ethereal extract of the original filtrate also gives a small amount of a crystalline product, which, on being recrystallised from water, melts at 150—151°. The substance is soluble in alcohol, ethyl acetate, or acetic acid, but insoluble in chloroform, benzene, or light petroleum. The yield is about 70 per cent. of the theoretical. Two different preparations were analysed (Found *: C = 63·2, 62·8; H = 6·6, 6·7. M.W. † = 374, 368, 364. $C_{19}H_{22}O_7$ requires C = 63·0; H = 6·1 per cent. M.W. = 362).

The *sodium* salt is prepared in the usual way by means of sodium hydrogen carbonate. It crystallises from water in microscopic, prismatic needles, which char and decompose at 328—333°, without melting (Found: Na = 10·1. $C_{19}H_{21}O_7Na$ requires Na = 9·4 per cent.).

The *methyl* ester, prepared by the action of an ethereal solution of diazomethane (from 14 c.c. of nitrosomethylurethane) on 1 gram of the acid dissolved in ether, crystallises from alcohol in needles, which melt at 119°, carbon dioxide being evolved (Found ‡: C = 63·8; H = 6·8. $C_{20}H_{24}O_7$ requires C = 63·8; H = 6·4 per cent.). On warming with dilute alkali, the acid is regenerated (m. p. 150—151).

3 : 4 : 2′ : 4′ : 6′-*Pentamethoxydiphenylacetic Acid* (XII).

3 : 4 : 2′ : 4′ : 6′-*Pentamethoxydiphenylmethyl chloride* was prepared by heating 8 grams of 3 : 4 : 2′ : 4′ : 6′-pentamethoxydiphenylcarbinol § (Kostanecki and Lampe, *Ber.*, 1906, **39**, 4015) on a water-bath for three hours with 8 grams of thionyl chloride. As much as possible of the unchanged thionyl chloride was distilled off under diminished pressure, the last traces being removed by warming with 3 c.c. of formic acid (compare H. Meyer, *Monatsh.*, 1901, **22**, 428). The residue crystallises from dry benzene in long, prismatic needles, which melt at 69°. The yield is 94 per cent.

* Dried at 110°.

† By titration with *N*/10-potassium hydroxide and phenolphthalein.

‡ Dried over phosphoric oxide in a vacuum.

§ The 3 : 4 : 2′ : 4′ : 6′-pentamethoxybenzophenone (Kostanecki and Tambor, *Ber.*, 1906, **39**, 4023) required was prepared by the condensation of phloroglucinol trimethyl ether and veratroyl chloride. The latter substance is described as an oil boiling at 270–277° (Kostanecki and Tambor, *loc. cit.*, who used phosphorus pentachloride) and as a crystalline solid, melting at 68–69° (Ryan and Walsh, *loc. cit.*, who used thionyl chloride). I have prepared veratroyl chloride by both these methods and find that the addition of a small crystal of Ryan and Walsh's substance immediately causes the product prepared by Kostanecki and Tambor's method to solidify. Both these preparations melt at 68–69°.

of the theoretical (Found: Cl = 10·2. $C_{18}H_{21}O_5Cl$ requires Cl = 9·9 per cent.).

Twelve grams of the chloride dissolved in dry ether (Grignard) are heated on a water-bath with 2 grams of "activated" magnesium (Baeyer, *Ber.*, 1905, **38**, 2759), dry carbon dioxide being passed through the solution for three and a-half hours. The solution turns red and becomes filled with a flocculent, yellow product, which reaches its maximum in about three hours. The ether is evaporated, and the residue first diluted with ice-water and subsequently decomposed with 40 c.c. of carefully cooled concentrated hydrochloric acid. The yellow, brittle solid is warmed with 75 c.c. of a solution consisting of 50 c.c. of concentrated ammonia and 50 c.c. of water, when the greater part dissolves. The filtrate is acidified with dilute sulphuric acid and the precipitate crystallised from water with the aid of animal charcoal. Long, silky needles are obtained, which melt at 150—151°, carbon dioxide being evolved. This melting point is not depressed when the substance is mixed with the acid prepared from Kostanecki and Lampe's methylated reduction product. The yield is 74 per cent. of the theoretical (Found*: C = 62·8; H = 6·6. Calc.: C = 63·0; H = 6·1 per cent.).

An ethereal solution of 1 gram of the acid gives on treatment with ethereal diazomethane (from 13 c.c. of nitrosomethylurethane) the methyl ester previously described. It crystallises from alcohol in needles melting at 119°, and a mixture of the two preparations melts at the same temperature (Found†: C = 63·5; H = 6·7. Calc.: C = 63·8; H = 6·4 per cent.). On warming with dilute alkali, the original acid is regenerated (m. p. 150—151°).

The author is indebted to the Colston Society of the University of Bristol for a grant which has covered the expenses of this research. He also wishes to express his thanks to Professor Ryan for his consent to the preparation of some of the substances described in this paper.

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UNIVERSITY OF BRISTOL. [*Received July 16th*, 1920.]

* Dried at 110°. † Dried over paraffin in a vacuum.

CVIII.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part II. The Effect of Position-isomerism and Conjugation on Optical Activity among Aryl Derivatives of Amino- and Bisimino-camphor.*

By Bawa Kartar Singh, Dalip Singh, Guru Dutt, and Gopal Singh.

Deviations from Frankland's rule, as indicated among arylimino-camphor derivatives by Singh and Mazumdar (T., 1919, **115**, 566), extend also to the corresponding products of reduction, prepared in the manner described by Forster and Thornley (T., 1909, **95**, 942).

The molecular rotatory power of the new derivatives of phenylaminocamphor are tabulated below.

Table I.

Derivatives of phenylaminocamphor	$[M]_D$ in chloroform solution. Me(15)	Br(80)	OMe(31)
Ortho	179°	235°	272·2°
Meta	361	277·6	—
Para	265	288·9	186
	o<p<un*<m,	o<m<p<un,	p<o<un

The value of $[M]_D$ of phenylaminocamphor is 311°.

* Unsubstituted.

Table II.

Derivatives of phenylaminocamphor	$[M]_D$ in methyl-alcoholic solution. Me(15)	Br(80)	OMe(31)
Ortho	174°	230·2°	146·3°
Meta	198	207·9	—
Para	158	209·6	—
	p<o<m<un,	m<p<un<o,	o<un;

The value of $[M]_D$ of phenylaminocamphor is 229·8°. The mean temperature of the observations recorded in tables I and II was 16° to 23°.

The following conclusions may be drawn from the data given in tables I and II:

(1) The order of rotatory power as laid down by Frankland is not followed once in the above five cases.

(2) The difference in rotatory powers of *o*- and *p*-tolyl compounds is one and a-half times as large as that in the case of the bromophenyl derivatives in chloroform solution, although bromine is a heavier group than the methyl radicle.

(3) In no case has the para-compound the maximum rotation, whereas the ortho-, meta-, and the unsubstituted compound each has had the maximum rotatory power.

(4) The effect of solvent on the order of rotatory power of position isomerides is remarkable; the *o*-bromophenyl compound has the lowest value in chloroform, whereas it has the highest value in methyl alcohol.

(5) Cohen's rule is only followed in two cases in chloroform solution, but not in the remaining three cases.

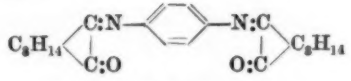
It is thus clear that we have as yet no rule which can apply to all the cases hitherto investigated, and the most important point which has emerged from this work is that the nature of the solvent plays a considerable part in the order of rotation of position-isomerides.

Apart from the irregularities which are disclosed when corresponding *o*-, *m*-, and *p*-derivatives are compared with the parent substance, it is found that in the case of derivatives of phenylaminocamphor there is no simple connexion between the nature of the substituting element or group and its influence on rotatory power. In the case of the ortho-compounds, arranged in the order of increasing rotatory power, the sequence of the substituent element or group is Me<Br<OMe<H in chloroform solution and OMe<Me<H<Br in methyl-alcoholic solution, whilst for meta-compounds the order is Br < H < Me in chloroform and Br<Me<H in methyl-alcoholic solution, and for para-compounds OMe<Me<Br<H in chloroform and Me<Br<H in methyl alcohol. It is also clear that there is no simple relation between the nature of solvent and the sequence of the substituent element or group on the order of rotatory power. Similar irregularities have already been pointed out in connexion with the derivatives of phenyliminocamphor (Singh and Mazumdar, *loc. cit.*).

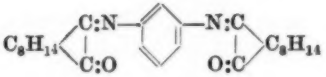
The marked effect of conjugated linkings on the optical rotation of compounds in the series under discussion was shown by Forster and Thorley (*loc. cit.*), particularly in connexion with *p*-phenylene-bisiminocamphor. Similar examples were given by Forster and Spinner (T., 1919, **115**, 889), and it is further emphasised by the following measurements in chloroform:

	$[M]_D$.	Difference of $[M]_D$.
o-Tolyliminocamphor	1183°	
		1004°
o-Tolylaminocamphor	179	
m-Tolyliminocamphor	1665	
		1304
m-Tolylaminocamphor	361	
p-Tolyliminocamphor	2177	
		1912
p-Tolylaminocamphor	265	
o-Bromophenyliminocamphor	1382	
		1146
o-Bromophenylaminocamphor	236	
m-Bromophenyliminocamphor	1338	
		1060
m-Bromophenylaminocamphor	278	
p-Bromophenyliminocamphor	1695	
		1406
p-Bromophenylaminocamphor	289	
ar-Tetrahydro-α-naphthyliminocamphor	1330	
		982
ar-Tetrahydro-α-naphthylaminocamphor	348	
o-Methoxyphenyliminocamphor	612	
		340
o-Methoxyphenylaminocamphor	272	
Camphanoquinoxaline	68	
		500
Camphanodihydroquinoxaline	−432	
m-Tolylenebisiminocamphor	1393	
		1039
m-Tolylenebisaminocamphor	354	

It is brought out very clearly also by reviewing the arrangement of double linkings in the structural formulæ for *p*- and *m*-phenylenebisiminocamphor and *m*-phenylenebisaminocamphor respectively, and comparing the molecular rotatory power in chloroform solution:



6096°



2660

435

This illustrates the effect of interrupting the conjugation in the benzene ring and at the junction with the camphor nucleus.

Experimental.

o-, m-, *and* p-*Tolylaminocamphors*, $C_8H_{14}\langle^{CH\cdot NH\cdot C_6H_4\cdot CH_3}_{CO}$.

These compounds, which were prepared by the action of zinc dust and potassium hydroxide on the corresponding imino-derivative, are very readily soluble in chloroform or benzene, less readily in methyl alcohol, ethyl alcohol, or acetone, and insoluble in water; they crystallise from hot alcohol in colourless prisms. The measurements of rotatory power were made by dissolving the stated

weight in 19·9 c.c. of the solvent and examining the solution in a 2-dcm. tube within half an hour.

The *ortho*-compound melts at 132—133° (Found: C=79·06; H=9·07. $C_{17}H_{23}ON$ requires C=79·37; H=8·95 per cent.).

Solvent.	Substance. Gram.	Temperature.	Time. Hours.	α.	$[\alpha]_D$.	$[M]_D$.
Methyl alcohol	0·0439	16°	—	+0·30°	+67·9°	+174·0°
"	"	17	38	0·26	58·9	150·4
Chloroform	0·0557	17	—	0·39	69·7	179·0
"	"	17	21	0·48	85·7	220·

The *meta*-compound melts at 83—84° (Found: C=79·14; H=9·0 per cent.).

Solvent.	Substance. Gram.	Temperature.	Time. Hours.	α_D.	$[\alpha]_D$.	$[M]_D$.
Methyl alcohol	0·0642	17°	—	+0·48°	+77·5°	+198·1°
"	"	17	14	0·53	83·7	215·1
Chloroform	0·0505	17	—	0·71	140·6	361·3
"	"	17	14	0·65	128·7	330·7

The *para*-compound melts at 82—84° (Found: C=79·34; H=8·99 per cent.).

Solvent.	Substance. Gram.	Temperature.	Time. Hours.	α_D.	$[\alpha]_D$.	$[M]_D$.
Methyl alcohol	0·0485	18°	—	+0·30°	+61·5°	+158·1°
"	"	18	20	0·28	57·5	146·8
Chloroform	0·0542	17	—	0·56	102·8	264·2
"	"	17	8	0·54	99·2	254·9

o-, m-, *and* p-*Bromophenylaminocamphor*, $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot C_6H_4Br\\ |\\ CO\end{matrix}$.

These are readily soluble in ether, chloroform, or benzene, sparingly so in methyl alcohol or ethyl alcohol, and insoluble in water; they crystallise from hot alcohol in colourless prisms or needles.

The *ortho*-compound melts at 148° (Found: C=59·51; H=6·21. $C_{16}H_{20}ONBr$ requires C=59·61; H=6·21 per cent.). The measurements of rotatory power, made as above, showed very slight mutarotation.

Solvent.	Substance. Gram.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·0404	19°	+0·31°	+76·3°	+245°
Methyl alcohol	0·0278	19	0·20	71·1	230

The *meta*-compound melts at 95° (Found: C=59·21; H=6·41 per cent.).

The rotatory-power determinations gave the following values without mutarotation:

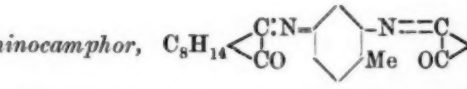
Solvent.	Substance. Gram.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·5655	19°	+0·49°	+86·2°	+278°
Methyl alcohol	0·0323	19	0·21	64·6	208

The *para*-compound melts at 105° (Found: C = 59·21; H = 6·35 per cent.).

Solvent.	Substance. Gram.	Temperature.	Time. Hours.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·0532	19°	—	+0·48°	+89·7°	+289°
,,	,,	19	24	0·50	93·5	300
Methyl alcohol	0·0359	19	—	0·23	65·1	209
,,	,,	19	24	0·24	67·8	218

For comparison with the foregoing substances, the following measurements were made with phenylaminocamphor:

Solvent.	Substance. Gram.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·0504	23	+0·65°	+128·3°	+311°
Methyl alcohol	0·0555	23	0·53	95	229·8

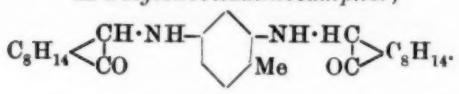
m-*Tolylenebisiminocamphor*, C_8H_{14}  C_8H_{14}.

One molecular proportion of *m*-tolylenediamine hydrochloride and two molecular proportions of camphorquinone were mixed with excess of fused sodium acetate and heated on the water-bath for two hours. The product was cooled, dissolved in a small quantity of alcohol, and precipitated by the addition of water. It crystallises from ether in yellowish-green needles melting at 172° (Found: N = 6·69. $C_{27}H_{34}O_2N_2$ requires N = 6·89 per cent.).

It is readily soluble in ethyl alcohol, methyl alcohol, ether, or chloroform, and insoluble in water. The rotatory-power determinations were carried out by dissolving the given weight of the substance in 100 c.c. of the solvent, with the following result, no mutarotation being observed:

Solvent.	Substance. Gram.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·0330	20°	+0·22°	+333·3°	+1393°
Methyl alcohol	0·0342	20	0·17	248·5	1038·7

m-*Tolylenebisaminocamphor*,

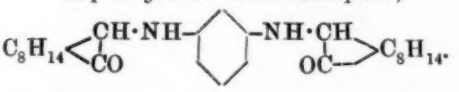


Reduction in this case was effected in the usual way by shaking an ethereal solution of *m*-tolylenebisiminocamphor with zinc dust and 10 per cent. potassium hydroxide in a closed bottle for three hours. The colourless residue left by the ether crystallised from ethyl alcohol in needles melting at 139° (Found: C=76·3; H=9·2. $C_{27}H_{38}O_2N_2$ requires C=76·09; H=9·2 per cent.).

The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Substance. Gram.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·0320	20°	+0·27°	+83·9°	+354°
Methyl alcohol	0·0292	20	0·26	91·6	386

m-*phenylenebisaminocamphor*,

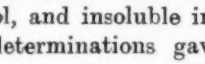


m-Phenylenebisiminocamphor (compare Singh and Mazumdar, *loc. cit.*) gave on reduction, as in the last case, m-*phenylenebisaminocamphor*, which crystallised from alcohol in colourless prisms melting at 163° (Found: C=76·2; H=8·1. $C_{26}H_{36}O_2N_2$ requires C=76·4; H=8·4 per cent.).

It is readily soluble in ether or chloroform, sparingly so in ethyl alcohol or methyl alcohol, and insoluble in water.

The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Substance. Gram.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·0250	20°	+0·38°	+151·2°	+435·5°
Methyl alcohol	0·0227	20	0·27	118·3	342·7

o-*Methoxyphenylaminocamphor*, 

o-Methoxyphenyliminocamphor (compare Singh and Mazumdar, *loc. cit.*), when reduced in the usual way, loses its colour, with the formation of o-*methoxyphenylaminocamphor*; this crystallises from alcohol in white needles melting at 148—149° (Found:

C=74·03; H=8·67. $C_{17}H_{23}O_2N$ requires C=74·45; H=8·76 per cent.).

It is readily soluble in chloroform or ether, less so in benzene, acetone, methyl alcohol, or ethyl alcohol, and insoluble in water.

The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Substance. Gram.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Methyl alcohol	0·2331	20°	+0·25°	+53·6°	+146·3°
Chloroform	0·2306	20	0·46	99·7	272·2

Camphanodihydroquinoxaline, $C_8H_{14}<\begin{matrix}CH\cdot NH\\ |\\ C=\!=N\end{matrix}>C_6H_4$.

Camphanoquinoxaline was reduced with stannous chloride and concentrated hydrochloric acid by heating for half an hour on the water-bath. On cooling, the stannichloride of camphanodihydroquinoxaline separated as a yellow, granular mass, which was collected, washed with hydrochloric acid, and treated with warm dilute potassium hydroxide, the *camphanodihydroquinoxaline* being extracted with ether; the colourless residue crystallised from hot alcohol in needles melting at 210—215° (Found: C=79·7; H=8·2. $C_{16}H_{20}N_2$ requires C=80·0; H=8·3 per cent.).

The rotatory-power determinations gave the following values:

Solvent.	Substance. Gram.	Temperature.	Time. Hours.	α_D.	$[\alpha]_D$.	$[M]_D$.
Chloroform	0·2276	20°	—	−0·80°	−175·7°	−421·68
„	„	29	20	−0·82	−180·0	−432·0

It is noteworthy that camphanodihydroquinoxaline has a fairly high lævorotatory power, whereas the parent substance, camphanoquinoxaline, possesses only a comparatively low dextrorotatory power, $[M]_D$ +68° (compare Singh and Mazumdar, *loc. cit.*).

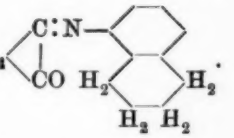
α- and β-Naphthylaminocamphor, $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot C_{10}H_7\\ |\\ CO\end{matrix}$.

α-Naphthylaminocamphor melted at 163—165°, and was identical with Forster and Spinners' compound (T., 1919, **115**, 891). The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Substance. Gram.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Methyl alcohol	0·3065	16·8°	+0·44°	+71·77°	+210·1°
Chloroform	0·2794	18	0·51	91·3	267·5

β-Naphthylaminocamphor, also prepared by Forster and Spinner (*loc. cit.*), was obtained in fine, silky needles melting at 156°. The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Substance. Gram.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Methyl alcohol	0·0565	18°	+0·71°	+125·0	+366·2°
Chloroform	0·0565	18	0·81	142·6	417·8

ar-*Tetrahydro-α-naphthyliminocamphor*, C_8H_{14}  .

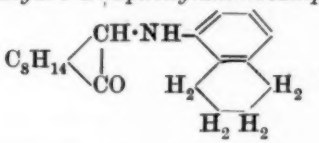
On mixing an alcoholic solution of camphorquinone with an aqueous solution of *ar*-tetrahydro-α-naphthylamine hydrochloride in the presence of excess of sodium acetate, an immediate reaction takes place, with the separation of a dark oil. The mixture is heated under reflux for two hours on the water-bath to complete the reaction. The product is precipitated by the addition of water, and crystallises from dilute alcohol in yellow needles melting at 132—134° (Found: C=80·93; H=8·45. $C_{20}H_{25}ON$ requires C=81·35; H=8·47 per cent.).

It is very readily soluble in chloroform, ether, benzene, or acetone, less so in methyl alcohol or ethyl alcohol, and insoluble in water.

The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Substance. Gram.	Temperature.	α_D.	$[\alpha]_D$.	$[M]_D$.
Methyl alcohol	0·1678	18°	+1·32°	+393·2°	+1159·9°
Chloroform	0·1608	18	1·45	450·9	1330·0

ar-*Tetrahydro-α-naphthylaminocamphor*,



ar-*Tetrahydro-α-naphthylaminocamphor* crystallises from hot alcohol in reddish-brown needles melting at 154—155° (Found: C=80·6; H=8·7. $C_{20}H_{27}ON$ requires C=80·8; H=9·1 per cent.).

It is very readily soluble in chloroform or ether, less readily so

in benzene or acetone, sparingly so in methyl alcohol or ethyl alcohol, and insoluble in water.

The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Substance. Gram.	Temperature.	α.	$[\alpha]_D$.	$[M]_D$.
Methyl alcohol	0·0548	20°	+0·12°	+109·5°	+325·2°
Chloroform	0·0809	20	0·19	117·1	347·8

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CIX.—*Ortho-para-isomerism in the Preparation of Diaminodiphenylmethane.*

By HAROLD KING.

IN the course of an investigation of the nitro-derivatives of diaminodiphenylmethane, prepared either from dianilinomethane or from anhydroformaldehydeaniline and aniline, it was found that the crude, distilled diaminodiphenylmethane was a mixture of the 4:4′- and 2:4′-derivatives in the proportion of about 9 to 1. By crystallising the nitration products, 2:2′-dinitro-4:4′-diaminodiphenylmethane was first isolated, and from the mother liquors a mononitro-derivative, which, on removal of the amino-groups, subsequent reduction, and acetylation, gave 4-*acetylaminodiphenylmethane*. The mononitro-derivative must have arisen from 2:4′-diaminodiphenylmethane present in the starting material, as was confirmed by the separation of the two isomeric bases and the mono-nitration of the unsymmetrical base.

EXPERIMENTAL.

Preparation of Diaminodiphenylmethane.

From Dianilinomethane.—Fifty grams of crystalline dianilinomethane were digested with 59 c.c. of aniline, 31 c.c. of concentrated hydrochloric acid, and 24 c.c. of water for twelve hours at 95°. The product was made alkaline and completely freed from aniline by steam distillation. The residual non-volatile base, after washing by agitating with fresh quantities of water, was distilled

under reduced pressure, yielding 33 grams of crude diaminodiphenylmethane, which boiled at 236—240°/11 mm.

From Anhydroformaldehydeaniline.—One hundred grams of solid anhydroformaldehydeaniline, 249 c.c. of aniline, 43 c.c. of water, and 130 c.c. of concentrated hydrochloric acid were mixed and heated on the water-bath for twelve hours. The crude, distilled aniline-free base boiled at 238—242°/15 mm., and amounted to 148·5 grams.

Nitration of Diaminodiphenylmethane and Isolation of 4-Nitro-2:4′-diaminodiphenylmethane.

Fifty grams of distilled diaminodiphenylmethane were nitrated by Benda's method (*Ber.*, 1912, **45**, 1787). The crude nitration product was collected and extracted once when dry with a limited volume of boiling alcohol. The insoluble solid consisted of 2:2′-dinitro-4:4′-diaminodiphenylmethane, and amounted to 60·5 grams, which is 83 per cent. of the theoretical yield. As the material soluble in alcohol could not be purified by further crystallisation, the solution was evaporated to dryness, and the residual solid, amounting to 14·4 grams, dissolved in hot 10 per cent. hydrochloric acid solution and fractionally precipitated by addition of 10 per cent. solution of ammonia. After removal of tarry matter, further addition of ammonia to the hot solution caused the separation of a crystalline precipitate, and eventually a point was reached at which a turbidity developed, due to the incipient formation of an oil. The crystalline material was collected, and consisted of 6·3 grams of almost pure 2:2′-dinitro-4:4′-diaminodiphenylmethane. The filtrate was now completely precipitated with ammonia, and, when cold, the crude 4-nitro-2:4′-diaminodiphenylmethane (4·3 grams) was collected. The total yield of dinitro-base was about 92 per cent., and of the crude mononitro-base 7 per cent.

Another experiment, in which Ehrlich and Bauer's method (*Ber.*, 1915, **48**, 502) of nitration was employed, furnished a 10 per cent. yield of crude mononitrodiaminodiphenylmethane.

4-Nitro-2:4′-diaminodiphenylmethane dissolves in about twenty-three parts of boiling alcohol, and crystallises in glistening, orange needles melting at 157—158° (corr.) (Found: C=64·4; H=5·5. $C_{13}H_{13}O_2N_3$ requires C=64·2; H=5·4 per cent.).

The *dihydrochloride* crystallises in microscopic, hexagonal-shaped leaflets melting and decomposing at 262° (corr.) (Found: Cl=22·3. $C_{13}H_{13}O_2N_3,2HCl$ requires Cl=22·4 per cent.).

The *diacetyl* derivative crystallises from acetic anhydride or

boiling methyl alcohol, in which it dissolves to the extent of 1·2 per cent. in pale buff-coloured, woolly needles melting at 239—240° (corr.) (Found: C=62·2; H=5·3. $C_{17}H_{17}O_4N_3$ requires C=62·4; H=5·2 per cent.).

The *tetra-acetyl* derivative obtained when the diacetyl derivative is boiled with excess of acetic anhydride is soluble in about one hundred times its weight of boiling alcohol, and separates in clear, oblique prisms melting at 201·5—202·5° (corr.) (Found: C=61·6; H=5·4. $C_{21}H_{21}O_6N_3$ requires C=61·3; H=5·1 per cent.).

4:3′-Dinitro-2:4′-diacetylaminodiphenylmethane.

4-Nitro-2:4′-diacetylaminodiphenylmethane (1·3 grams), when nitrated with a mixture of sulphuric and nitric acids, gave 1·45 grams of the crude dinitrated anilide. It was recrystallised twice from glacial acetic acid, yielding, finally, 1·15 grams. It dissolves in fifty volumes of the boiling solvent, and crystallises as a voluminous mass of golden needles melting at 264—265° (corr.). A mixture with the isomeric 3:3′-dinitro-4:4′-diacetylaminodiphenylmethane, which melts at 259—260° (uncorr.), melted at 233° (Found: C=55·3; H=4·4. $C_{17}H_{16}O_6N_4$ requires C=54·8; H=4·3 per cent.).

3′:4-Dinitro-2:4′-diaminodiphenylmethane.

The free aniline prepared from the above anilide, when recrystallised from boiling alcohol (twenty-four parts), separates in glistening, orange needles, very similar in appearance to 4-nitro-2:4′-diaminodiphenylmethane. It melts at 148·5—149·5° (corr.) (Found: C=54·5; H=4·2. $C_{13}H_{12}O_4N_4$ requires C=54·2; H=4·2 per cent.).

4-Acetylaminodiphenylmethane.

4-Nitro-2:4′-diaminodiphenylmethane was deprived of the amino-groups by the diazo-reaction, the product reduced, and acetylated. Purification by recrystallisation from alcohol gave the compound in the form of large, pearly leaflets melting at 128—129° (corr.), and a mixed melting point with 4-acetylaminodiphenylmethane, prepared from benzene and *p*-nitrobenzyl chloride by the Friedel and Crafts synthesis, followed by reduction and acetylation, showed no depression (Found: N=6·2. $C_{15}H_{15}ON$ requires N=6·2 per cent.).

Separation of 2:4′- and 4:4′-Diaminodiphenylmethanes.

(*a*) *Use of Benzylidene Derivative.*—Crude, distilled diaminodiphenylmethane (148·5 grams) was converted into its dibenzylidene derivative. The alcoholic mother liquors were evaporated to dryness, and the residual semi-solid material was digested on the water-bath for two hours with 200 c.c. of 10 per cent. hydrochloric acid. The product was extracted with ether, and the acid aqueous solution rendered alkaline with ammonia and similarly extracted with ether. In this way, on removal of the solvent, 22·5 grams of syrup were obtained, which, on distillation under diminished pressure, gave 12 grams of a pale yellow oil. On acetylation, a crude diacetylaminodiphenylmethane was obtained, which was fractionally crystallised from alcohol. 9·5 Grams of pure 2:4′-diacetylaminodiphenylmethane were obtained, representing a minimum content of 4·5 per cent. of the ortho-para-base in the original material. The separation is difficult, and is only possible when the acetylated product contains excess of the ortho-para-isomeride.

(*b*) *Use of differing Basicities.*—Seventy grams of crude, distilled diaminodiphenylmethane were dissolved in chloroform, and the solution was extracted thirty-two times by means of dilute sulphuric acid solution. Each extract contained 10 c.c. of 10 per cent. sulphuric acid solution diluted to such a volume as would keep the sparingly soluble sulphates in solution. In this way, solubility relationships were avoided, as attempts to separate the two bases by fractional crystallisation or precipitation of salts led to no result. The progress of the separation was followed by precipitating the acid fractions at intervals, by means of ammonia, and comparing the melting point of the acetyl derivatives with a mixed melting point with pure 4:4′-diacetylaminodiphenylmethane. By this means, it was found that the 2:4′-disubstituted base was concentrated in the last four extracts, which on acetylation gave 10·4 grams of solid material. This was fractionally crystallised from alcohol, when 5·0 grams of pure 2:4′-diacetylaminodiphenylmethane were obtained.

2:4′-Diacetylaminodiphenylmethane crystallises from boiling 95 per cent. alcohol (14 parts) in glistening, delicate, rectangular leaflets melting at 224—225° (corr.). It often melts at 209—210° (uncorr.), and if the molten contents are allowed to cool, it resolidifies, and then re-melts at 224°. Occasionally the substance becomes semi-transparent at 210°, and then clears and forms a definite meniscus at 223—224°. Zincke and Prentzell (*Ber.*, 1905, **38**, 4121), by recrystallisation from alcohol, obtained two modifications, white tablets melting at 208° and small needles melting

at 218°. The author has only once succeeded in reproducing the needle form, by inoculating a hot saturated solution of the anilide with the powdered, re-solidified material melting at 224°. Both forms separated simultaneously, the needle form in much the smaller proportion.

The identity of the 2:4′-diacetylaminodiphenylmethane was proved by direct comparison with a sample prepared by Staedel's method (*Annalen*, 1894, **283**, 162) from 2:4′-dinitrodiphenylmethane. Both showed the characteristic double melting point, and a mixture of the two showed no depression (Found: N=10·1. Calc.: N=10·1 per cent.).

2:4′-Diaminodiphenylmethane is readily soluble in hot benzene, but crystallises well from the cold solution in pearly leaflets. It melts at 88—89° (corr.) and boils at 222°/9 mm.

The *dibenzylidene* derivative is readily soluble in ether, and is precipitated on addition of light petroleum as an oil.

4:4′-Diaminodiphenylmethane, free from the isomeride, is best prepared through the intermediary of the dibenzylidene derivative. It crystallises well from benzene in clusters of rectangular plates melting at 92—93° (corr.) and boiling at 232°/9 mm.

4:4′-*Diamino*-2:2′-*azoxydiphenylmethane.*

Pure 2:2′-dinitro-4:4′-diaminodiphenylmethane (1 gram) was suspended in 20 c.c. of alcohol, and 4 grams of crystalline, hydrated sodium sulphide, dissolved in 4 c.c. of water, were added. The solution was boiled for half an hour, and, when cold, the product, which separated in glistening, orange needles, was collected. The yield was 0·45 gram.

4:4′-Diamino-2:2′-azoxydiphenylmethane melts and decomposes at 265° (corr.) (Duval, *Compt. rend.*, 1905, **141**, 198, gives 272°). The only solvent at all suitable for its recrystallisation is pyridine (Found: C=64·9; H=5·3. Calc.: C=65·0; H=5·0 per cent.).

It forms a stable *dihydrochloride* crystallising in microscopic, six-sided leaflets, which are readily soluble in water without separation of the base. It has no definite melting point (Found: H_2O=8·6; Cl=20·8. $C_{13}H_{12}ON_4,2HCl,1\frac{1}{2}H_2O$ requires H_2O=7·9; Cl=20·8 per cent.).

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CX.—*Experiments on Halogenation. The Direct Displacement of Negative Groups by Halogen in the Aromatic Series. Part I. The Displacement of the Nitro-group by Bromine.*

By Surendra Nath Dhar.

In the series of which this paper is Part I, it is proposed to investigate the mechanism and conditions which lead to the direct displacement of negative groups by halogen atoms when such groups are attached to the aromatic nucleus, because, although several instances have been recorded of the occurrence of this type of reaction, no systematic study of it appears to have been made. It is evident that if a change of this kind could be definitely controlled and its course clearly established, it would serve as a valuable means for preparing certain aromatic derivatives not otherwise easily obtained.

In the first instance, therefore, it is intended to record certain experiments which have been carried out in connexion with the displacement of nitro-groups by bromine, a change which appears to have been first noted by Kekulé (*Annalen*, 1866, **137**, 169), when he obtained tri-, tetra-, and penta-bromobenzene by heating nitrobenzene with bromine in a sealed tube. Other instances of a similar character have since been published; thus, Meyer (*Monatsh.*, 1915, **86**, 723) found that nitrobenzene under the influence of thionyl chloride gives chlorobenzene, and that *m*-dinitrobenzene when treated with chlorine is converted first into *m*-chloronitrobenzene and finally into *m*-dichlorobenzene (D.R.-P. 108165). Picric acid gives with bromine the same bromodinitrophenol as is obtained when dinitrophenol is brominated (Armstrong, *J. Soc. Dyers*, 1885, **1**, 85). Other instances of the displacement of nitro-groups by halogens in the benzene as well as in the naphthalene series have been recorded by Lobry de Bruyn and Leent (*Rec. trav. chim.*, 1896, **15**, 84), Atterberg (*Ber.*, 1876, **9**, 316, 926, 1734; 1877, **10**, 1841), and Jolin (*Bull. Soc. chim.*, 1877, [ii], **28**, 514). Direct displacement of the nitro-group has also been noticed in the anthracene series. Thus 1-nitroanthraquinone is converted into 1-chloroanthraquinone through the agency of chlorine, and 1:5-dinitroanthraquinone into the 1:5-dichloro-derivative by the same process (D.R.-P. 252578).

In the present paper are described experiments dealing with the behaviour of certain typical nitro-derivatives of benzene,

naphthalene, anthracene, xanthone, and coumarin towards bromine at a high temperature, when the bromine is present in the proportion of one molecule of the halogen to each nitro-group. These experiments were carried out with the object of settling one of the fundamental points in connexion with the reaction, namely, the reason why it does not stop when all the nitro-groups, or all such as are capable of displacement, are substituted by the halogen, but in many cases proceeds further, leading to the formation of higher halogenated derivatives. Moreover, preliminary experiments showed that not only did further halogenation take place with remarkable ease, but that it was possible by the aid of this reaction to prepare halogen derivatives which could not be obtained by the direct halogenation under known conditions. Examples of this kind are given in the experimental part, the best being that supplied by the formation of octabromoxanthone (p. 999).

It is evident, therefore, that in this reaction some product is formed which acts as a very much more powerful halogenating agent than the halogen itself, and it is thought that this substance may well be the nitro-derivative of bromine, which might be formed in accordance with the equation

$$RHNO_2 + Br_2 \longrightarrow RHBr + BrNO_2,$$

the reaction being completed in accordance with the equation

$$RHBr + BrNO_2 \longrightarrow RBr_2 + HNO_2.$$

If this is the true explanation of the course of the reaction, it follows that a trinitro-derivative when treated with three molecules of bromine should, if a sufficient number of hydrogen atoms are present in the nitro-derivative, yield a compound containing six atoms of bromine, and that this is actually the case is shown by the behaviour of trinitrotoluene, which is transformed under these conditions into pentabromobenzyl bromide:

(1) $C_6H_2Me(NO_2)_3 + 3Br_2 \longrightarrow C_6H_2MeBr_3 + 3BrNO_2,$

(2) $C_6H_2MeBr_3 + 3BrNO_2 \longrightarrow C_6Br_5\cdot CH_2Br + 3HNO_2.$

It may be added that this view is supported by the fact that in this and other similar cases the halogenation does not proceed further, even though excess of bromine is used. Similarly, both 1:5- and 1:8-dinitronaphthalene when treated with two molecular proportions of bromine yield the same tetrabromonaphthalene, which must therefore be the 1:(4):5:8-compound, the formation of the substance being in complete accord with the views expressed above.

It would be difficult to predict the reactions which might occur between the substance $BrNO_2$ and phenols, but it is reasonable to suppose that one of them would be the displacement of the

hydroxyl by bromine and the formation of nitric acid, in accordance with the equation

$$R{\cdot}OH + BrNO_2 \longrightarrow RBr + HNO_3.$$

It is therefore interesting to note that when picric acid is treated with three molecular proportions of bromine, it is converted into hexabromobenzene, although tetrabromo- and pentabromo-phenol are also produced. It is probable, therefore, that the reaction takes place chiefly in accordance with the equations

(1) $C_6H_2(OH)(NO_2)_3 + 3Br_2 \longrightarrow C_6H_2(OH)Br_3 + 3BrNO_2$,
(2) $C_6H_2(OH)Br_3 + 3BrNO_2 \longrightarrow C_6Br_6 + HNO_3 + 2HNO_2$.

It is evident that both tetrabromo- and pentabromo-phenol are intermediate products in the reaction, because the yield of hexabromobenzene increases with the temperature of the reaction.

Although in the instances given above the displacement of the nitro-groups and subsequent bromination proceeds smoothly and completely, yet it is evident that the completion of the reaction must depend on two main factors, namely, (*a*) the stability of the nitro-group, and (*b*) the tendency for hydrogen atoms present in the molecule of the aromatic substance to be displaced by bromine. It is to be expected that experiment would reveal the operation of these two factors, and that instances would be found in which the reaction would leave nitro-groups in stable positions unattacked and in which the further entrance of bromine atoms would be inhibited. Actually, the experiments carried out with nitro-derivatives of xanthone and coumarin have supplied admirable examples of the operation of both factors, although in every case the course of the reaction can be explained by the general equations given above.

It may be added that all the nitro-compounds mentioned in this paper, excepting those of the coumarin series, have been treated with bromine in the usual solvents, such as acetic acid or nitrobenzene, without result. Compounds of the coumarin series do, however, yield bromo-derivatives under these conditions (see p. 1000). Thus both α_1- and β_1-tetranitroxanthone give only dibromodinitroxanthone, and 3:6-dinitrocoumarin gives 3-bromo-6-nitrocoumarin when treated with four and two molecules of bromine respectively. On the other hand, α_2-tetranitroxanthone gives tetrabromoxanthone, and 1:3- and 1:5-dinitroanthraquinone give 1:3- and 1:5-dibromoanthraquinone, respectively, under the same experimental conditions.

Further experiments, carried out under different conditions, will be necessary in order to determine the order in which the nitro-groups are displaced, and it is hoped that in this way valuable

evidence respecting the position-stability of this group will be forthcoming. Even in the present preliminary experiments, however, there is clear evidence of the remarkabl stability conferred on nitro-groups occupying certain positions in an aromatic nucleus. It has been pointed out, for example, by Jordan and Thorpe (T., 1915, **107**, 395) that whereas a nitro-group can be introduced into position 6 of the coumarin molecule with remarkable ease, it is a matter of considerable difficulty to introduce this group into position 3. The present experiments show that a nitro-group in position 6 cannot be displaced by bromine, and that one in position 3 is readily displaced. For example, 6-nitrocoumarin with one molecule of bromine yields 3-bromo-6-nitrocoumarin, and 3:6-dinitrocoumarin with two molecules of bromine gives the same 3-bromo-6-nitrocoumarin. Even when the last-named reaction is carried out at a high temperature, the nitro-group is not displaced, the final product being a tetrabromonitrocoumarin.

EXPERIMENTAL.

Benzene Series. The Bromination of Picric Acid.

Three grams of picric acid and 2 c.c. of bromine (3 mols.), together with a trace of iodine, were heated in a sealed tube at 220—250° for six hours. The crude product (4 grams), when treated with dilute alkali, yielded an insoluble residue which, when collected and recrystallised from benzene, was found to be hexabromobenzene, melting at 315° (Found: Br = 86·87. Calc.: Br = 86·96 per cent.). The precipitate obtained when the alkaline filtrate was acidified, when fractionally recrystallised from alcohol, yielded two substances. The less readily soluble one melted at 225°, and proved to be pentabromophenol (Found: Br = 81·61.* Calc.: Br = 81·81 per cent.), and the more readily soluble one, which melted at 120°, was tetrabromophenol (Found: Br = 78·53.* Calc.: Br = 78·03 per cent.).

The same products are obtained when the reaction is carried out at either 130° or at 300°, but the amount of hexabromobenzene formed is much greater at the higher temperature.

The Bromination of 2:4:6-*Trinitrotoluene.*

Pentabromobenzyl Bromide.—Three grams of 2:4:6-trinitrotoluene, 2 c.c. of bromine (3 mols.), and a trace of iodine were heated in a sealed tube at 200° for eight hours. The crude pro-

* All halogen estimations were made by Robertson's method (T., 1915, 107, 902).

duct (2·5 grams), after being washed with dilute alkali, was crystallised from benzene, when it yielded slender, white needles melting at 320° (Found: Br = 84·53. $C_7H_2Br_6$ requires Br = 84·80 per cent.). Pentabromobenzyl bromide is sparingly soluble in alcohol, and no precipitate of silver bromide is formed when its solution is treated with freshly precipitated silver hydroxide or alcoholic silver nitrate solution. It appears to be a remarkably stable substance, since it is not oxidised to pentabromobenzoic acid either by alkaline permanganate or by nitric acid in a sealed tube. It remains unchanged when heated in a sealed tube with bromine.

Pentabromobenzyl Alcohol.—This substance was obtained by heating a mixture of 1 gram of pentabromobenzyl bromide, 5 c.c. of absolute alcohol, and 2 grams of potassium acetate in a sealed tube at 200° for eight hours. It crystallises from alcohol in slender needles melting at 175° (Found: Br = 79·82. $C_7H_3OBr_5$ requires Br = 79·52 per cent.). The compound is sparingly soluble in water, but dissolves readily in alcohol. It sublimes in colourless needles when heated at 100°.

Naphthalene Series. The Bromination of 1:5- *and of* 1:8-*Dinitronaphthalene.*

1:(4):5:8-*Tetrabromonaphthalene.*—Five grams of 1:5-dinitronaphthalene mixed with 2·5 c.c. of bromine (2 mols.) and a trace of iodine were heated in a sealed tube at 200° for five hours. The crude product (6 grams) crystallised from benzene in colourless needles melting at 308°, and the same compound is also obtained from 1:8-dinitronaphthalene under similar conditions (Found: Br = 71·88. $C_{10}H_4Br_4$ requires Br = 72·06 per cent.).

1:(4):5:8-*Tetrabromomononitronaphthalene* was obtained by treating the above compound with concentrated sulphuric acid and nitric acid (D 1·42). For 1 gram of substance, 50 c.c. of each acid were used. A yellow precipitate was obtained on keeping the mixture overnight. The substance melts and decomposes at 220° (Found: N = 2·83. $C_{10}H_3O_2NBr_4$ requires N = 2·86 per cent.).

Hexabromonaphthalene.—This compound was prepared by heating 1·5 grams of 1:2:5:8-tetranitronaphthalene with 1 c.c. of bromine (4 mols.) and a trace of iodine in a sealed tube at 220° for twenty hours. The crude product (about 2 grams), after being washed with dilute aqueous alkali hydroxide, crystallised from benzene in white needles melting at 280—285° (Found: Br = 79·60. $C_{10}H_2Br_6$ requires Br = 79·73 per cent.).

1:3:5:8-*Tetrabromonaphthalene.*—This substance was obtained by heating a mixture of 2 grams of 1:3:5:8-tetranitronaphthalene,

1·5 c.c. of bromine (4 mols.), and a trace of iodine in a sealed tube at 220° for twenty hours. The crude product (2·5 grams), after being washed with cold aqueous alkali hydroxide, crystallised from benzene in white needles melting at 310° (Found: Br = 72·13. $C_{10}H_4Br_4$ requires Br = 72·06 per cent.).

1 : 3 : 5 : 8-*Tetrabromonitronaphthalene.*—Half a gram of the tetrabromo-compound was dissolved in 50 c.c. of concentrated sulphuric acid, 50 c.c. of nitric acid (D 1·42) were added, and the solution was heated over the steam-bath for one hour. When cold, a yellowish-brown precipitate was obtained by pouring the solution into water; this was collected and washed with water. The substance melts at 205° and does not decompose even at 280° (Found: N = 2·76. $C_{10}H_3O_2NBr_4$ requires N = 2·86 per cent.).

1 : 2 : 6 : 8-*Tetrabromonaphthalene.*—This substance was obtained by heating 1·5 grams of 1 : 2 : 6 : 8-tetranitronaphthalene (p. 1004) with 1 c.c. of bromine (4 mols.) and a trace of iodine in a sealed tube at 220° for twenty hours. The substance was purified and crystallised, as in the case of hexabromonaphthalene, and obtained in yellowish-white, shining needles melting at above 315° (Found: Br = 72·26. $C_{10}H_4Br_4$ requires Br = 72·06 per cent.).

1 : 2 : 6 : 8-*Tetrabromonitronaphthalene* was obtained by nitrating the above tetrabromo-compound, as in the case of the 1 : 3 : 5 : 8-tetrabromo-compound. A brownish-yellow substance was obtained which melted at 230° (Found: N = 2·64. $C_{10}H_3O_2NBr_4$ requires N = 2·86 per cent.).

1 : 3 : 6 : 8-*Tetrabromonaphthalene.*—This was obtained by heating a mixture of 2 grams of 1 : 3 : 6 : 8-tetranitronaphthalene, 1·5 c.c. of bromine (4 mols.), and a trace of iodine in a sealed tube at 220° for twenty hours. White needles, melting at above 315°, were obtained by purifying the crude product (2 grams), as before (Found: Br = 71·74. $C_{10}H_4Br_4$ requires Br = 72·06 per cent.).

1 : 3 : 6 : 8-*Tetrabromonitronaphthalene* was obtained as a brownish-yellow powder by nitrating the tetrabromo-compound, as in the previous cases. The substance melts at 210° (Found: N = 2·77. $C_{10}H_3O_2NBr_4$ requires N = 2·86 per cent.).

Xanthone Series. The Bromination of Tetranitroxanthones.

In the following experiments a large excess of bromine was used, because preliminary experiments had shown that variation in the amount of halogen beyond the theoretical and in the temperature conditions did not affect the result.

Dibromodinitroxanthone was obtained by heating a mixture of

2 grams of α_1-tetranitroxanthone,* 3 c.c. of bromine (11 mols.), and a trace of iodine in a sealed tube at 300° for twenty-six hours. It crystallises from benzene (2 grams) in colourless needles melting at 265°. The same compound was obtained from β_1-tetranitroxanthone * under similar conditions (Found: Br = 36·22; N = 6·16. $C_{13}H_4O_6N_2Br_2$ requires Br = 36·08; N = 6·30 per cent.).

Tetrabromoxanthone.—This substance (about 3 grams) was obtained by heating a mixture of 2·5 grams of α_2-tetranitroxanthone,* 4 c.c. of bromine (more than 11 mols.), and a trace of iodine in a sealed tube at 300° for twenty-six hours. It is isolated from its solution in benzene (in which it is very readily soluble) as an amorphous, yellow solid melting at 255° (Found: Br = 62·36. $C_{13}H_4O_2Br_4$ requires Br = 62·50 per cent.). The compound is insoluble in alcohol and soluble in pyridine or acetic acid, but does not crystallise from either of these solvents. It is evidently different from the tetrabromoxanthone previously described (T., 1916, **109**, 746), because it cannot be converted into a dinitro-derivative on nitration.

Hexabromoxanthone.—This compound (about 4 grams) was prepared by heating 2·5 grams of β_2-tetranitroxanthone * with 4 c.c. of bromine (more than 11 mols.) and a trace of iodine in a sealed tube at 200° for thirty hours. It crystallises from benzene in slender, yellow needles melting at 288° (Found: Br = 72·01. $C_{13}H_2O_2Br_6$ requires Br = 71·63 per cent.). This compound is evidently different from that previously described (T., 1916, **109**, 748), because it does not yield a colouring matter when heated with aniline and a trace of copper powder.

Octabromoxanthone.—One gram of tetrabromodinitroxanthone (*loc. cit.*), 3 c.c. of bromine (36 mols.), and a trace of iodine were heated in a sealed tube at 300° for thirty-six hours. The product crystallised from benzene in slender, colourless needles melting at above 315° (Found: Br = 77·57. $C_{13}O_2Br_8$ requires Br = 77·31 per cent.).

Anthraquinone Series.

1:3-Dibromoanthraquinone was obtained by heating 2·2 grams of 1:3-dinitroanthraquinone, 1 c.c. of bromine (2 mols.), and a trace of iodine in a sealed tube at 200—250° for seven hours, and at 290° for a further hour. It crystallises from alcohol in canary-yellow needles melting at 210°, as stated by Ullmann and Eiser (*Ber.*, 1916, **49**, 2154) (Found: Br = 44·16. Calc.: Br = 43·71 per cent.).

* The new tetranitroxanthones mentioned in this paper will be described in a later communication.

1:5-Dibromoanthraquinone was obtained by heating 5 grams of 1:5-dinitroanthraquinone, 2 c.c. of bromine (2 mols.), and a trace of iodine in a sealed tube at 300° for four hours. The substance crystallises from benzene in pale yellow needles melting at above 320° (Found: Br = 43·48. Calc.: Br = 43·71 per cent.).

Coumarin Series.

3-*Bromo*-6-*nitrocoumarin*.—Three grams of 6-nitrocoumarin were heated with 2 c.c. of bromine (3 mols.) and a trace of iodine in a sealed tube at 130° for eight hours. The crude product (3·5 grams), after being washed with water, crystallised from alcohol in colourless needles melting at 215° (Found: Br = 29·96; N = 5·26. Calc.: Br = 29·63; N = 5·18 per cent.).

This compound is also obtained when 3:6-dinitrocoumarin is treated in a similar manner, or when 6-nitrocoumarin is heated in an open tube with bromine in acetic acid solution.

3:8-*Dibromo*-6-*nitrocoumarin*.—This substance was prepared by heating a solution of 4·5 grams of 3:6-dinitrocoumarin in 10 c.c. of acetic acid with 4 c.c. of bromine and a trace of iodine on a sand-bath for twenty hours. The product, after being washed with alcohol, crystallised from benzene in white needles melting at 220° (Found: Br = 45·89; N = 4·19. $C_9H_3O_4NBr_2$ requires Br = 45·84; N = 4·01 per cent.).

3:8:?-*Tribromo*-6-*nitrocoumarin*.—This compound was prepared by heating a mixture of 3 grams of 3:6-dinitrocoumarin, 2 c.c. of bromine (3 mols.), and a trace of iodine in a sealed tube at 180° for six hours. The crude product was purified by solution in cold aqueous alkali hydroxide, precipitation by dilute hydrochloric acid, and crystallisation from alcohol; it melts at 200—205° (Found: Br = 56·46; N = 2·77. $C_9H_2O_4NBr_3$ requires Br = 56·08; N = 3·26 per cent.). In this reaction a second product was formed which was insoluble in alkali hydroxide, and proved to be tetrabromonitrocoumarin (see below).

3-*Bromo*-6:8-*dinitrocoumarin* was obtained by heating 1·5 grams of 3:6:8-trinitrocoumarin dissolved in 5 c.c. of acetic acid with 2 c.c. of bromine and a trace of iodine on a sand-bath for twenty hours. The crude product, after being washed with cold aqueous alkali hydroxide, separated from alcohol as a yellowish-white solid melting at 130—135° (Found: Br = 25·82; N = 8·48. $C_9H_3O_6N_2Br$ requires Br = 25·40; N = 8·87 per cent.).

3:8:?:?-*Tetrabromo*-6-*nitrocoumarin*.—A mixture of 1·5 grams of 3:6:8-trinitrocoumarin with 1 c.c. of bromine (4 mols.) and a trace of iodine was heated in a sealed tube at 160° for six hours.

After being washed with dilute alkali, the product crystallised from alcohol in pale yellow needles melting at 260° (Found: Br = 63·29; N = 2·58. $C_9HO_4NBr_4$ requires Br = 63·10; N = 2·79 per cent.).

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CXI.—*Some Nitro-derivatives of Naphthalene and Anthraquinone.*

By Surendra Nath Dhar.

The present study was undertaken mainly with the view of preparing some nitro-compounds for halogenation in the manner dealt with in the previous paper. One remarkable fact has, however, been brought to light in connexion with the nitration of anthraquinone.

It is well known that when anthraquinone is nitrated, a mixture of dinitroanthraquinones is formed, and from such a mixture the nitro-compounds can be separated only with very great difficulty, using solvents such as acetone, pyridine, etc. By this method, only the following dinitroanthraquinones have been isolated from different mixtures: 1:5-, 1:6-, 1:7-, 1:8-, 2:6-, and 2:7- (D.R.-P. 167699).

It will be seen that, of the ten possible dinitro-compounds, the 1:2-, 1:3-, 1:4-, and 2:3-derivatives are missing. It is natural to suspect that some of these four isomerides might be left undetected in the mixtures, because of the unsatisfactory method of separation. It was therefore thought that the new method of bromination might help in detecting the unknown dinitro-compounds, if any. This expectation has been fulfilled.

A mixture of dinitroanthraquinones, obtained by nitrating anthraquinone by the ordinary method, was treated with bromine in a sealed tube, and the product was found to be a mixture of

1:2- (m. p. 268°), 1:3- (m. p. 210°), 1:5- (m. p. above 360°), and 2:6- (m. p. 285°) dibromoanthraquinones.

Attempts were then made to isolate the corresponding four dinitro-compounds. As a result of nitration under different conditions with different proportions of nitric and sulphuric acids, four dinitro-compounds have actually been obtained, but only two of them have been identified, and characterised as 1:5- and 1:3-dinitroanthraquinones respectively.

By the nitration of 1:8-dinitronaphthalene, Will (*Ber.*, 1895, **28**, 378) obtained only one of the two possible tetranitronaphthalenes, and characterised it as the 1:3:6:8-tetranitro-derivative; but in the present work both the tetranitro-compounds have been isolated, so that the new compound is necessarily 1:2:6:8-*tetranitronaphthalene*. Two *trinitro-β-naphthoic acids* have been obtained by the nitration of β-naphthoic acid.

It may here be stated that nitric acid has been found to be a useful solvent for nitro-compounds in general. By using this, not only are costly solvents avoided, but the separation of different nitro-compounds and their purification are accomplished with very great ease.

Experimental.

Anthraquinone Series.

Ten grams of anthraquinone were added gradually to a mixture of 250 grams of concentrated sulphuric acid and 250 grams of nitric acid (D 1·42) with shaking. The solution was kept over the steam-bath for about an hour, when yellow needles were obtained, which were collected over asbestos. The substance melted at 312—317°, and was found to be a mixture of dinitro-compounds. It was heated with two molecular proportions of bromine and a trace of iodine in a sealed tube for six hours between 250° and 300°. From the product, four different dibromoanthraquinones were separated by means of laborious fractional crystallisation. The crude product yielded an insoluble residue when boiled with alcohol. From the alcoholic solution two substances separated on fractional crystallisation. The less soluble one melted at 268° and proved to be 1:2-dibromoanthraquinone (Found: Br=44·21. Calc.: Br=43·71 per cent.), and the more readily soluble one, which melted at 210°, to be 1:3-*dibromoanthraquinone* (Found: Br=43·96). The insoluble residue yielded two other substances when fractionally crystallised from benzene. The more readily soluble one melted at 285°, and was 2:6-dibromoanthraquinone (Found: Br=43·98), and the less soluble one, which did

not melt up to 360°, was 1:5-dibromoanthraquinone (Found: Br=44·87).

Twenty-five grams of anthraquinone (sublimed) were mixed with concentrated sulphuric acid in a mortar, and the mixture was washed with sulphuric acid into a large flask. A further quantity of sulphuric acid was added to make the total amount of acid 300 c.c., and 400 c.c. of nitric acid were then added to the mixture. The flask was kept over the steam-bath for six hours, when yellow crystals precipitated. These were filtered over asbestos and washed with nitric acid and then with water. The substance was further purified by boiling with nitric acid. It did not melt up to 360°, and was identified as 1:5-dinitroanthraquinone (Found: N=9·31. Calc.: N=9·39 per cent.).

When boiled with sodium methoxide, it gave a dimethoxy-compound which melted at 236° (1:5-dimethoxyanthraquinone melts at 236° (D.R.-P. 167699), and when heated in a sealed tube with bromine and iodine a dibromo-compound was obtained which did not melt up to 300°.

1:3-*Dinitroanthraquinone.*—From the filtrate and washings of 1:5-dinitroanthraquinone another dinitro-compound was obtained by precipitation with water. It crystallised from nitric acid in yellow needles (5 grams) melting at 240° (Found: N=4·2. $C_{14}H_6O_6N_2$ requires N=9·39 per cent.).

When boiled with sodium methoxide it gave 1:3-dimethoxy-anthraquinone melting at 155° (Graebe, *Annalen*, 1906, **349**, 230, gives 150—153°).

3-*Nitro*-1-*aminoanthraquinone.*—1 : 3-Dinitroanthraquinone was reduced with alcoholic ammonium sulphide in the usual way. For each gram of the nitro-compound, 50 to 75 c.c. of alcohol and 20 to 25 c.c. of ammonia were required. The nitroamino-compound crystallised from alcohol in deep red needles which melted at 265° (Found: N=10·48. $C_{14}H_8O_4N_2$ requires N=10·45 per cent.).

3-*Nitroanthraquinone*-1-*azo*-β-*naphthol.*—The nitroamino-compound was diazotised in the usual way and combined with β-naphthol. The product separated from alcohol as a deep red, amorphous substance melting at 235—240° (Found: N=9·98. $C_{24}H_{13}O_5N_3$ requires N=9·92 per cent.).

3-Nitro-1-hydroxyanthraquinone was obtained by diazotising the nitro-amino-compound and warming the solution over the steam-bath for ten hours. It separated as a brick-red, amorphous powder melting at 240° (R. Scholl, *Ber.*, 1904, **37**, 4435, gives 247—248°) (Found: N=5·01. Calc.: N=5·20 per cent.).

Very small amounts of two other dinitro-compounds were

obtained from the nitric acid filtrates from 1:5- and 1:3-dinitroanthraquinones, and they are under investigation.

Nitration of both 1:5- and 1:3-dinitroanthraquinone was tried with mixtures of sulphuric and fuming nitric acids in various proportions by boiling over a sand-bath under reflux, but in each case the substance decomposed completely.

Naphthalene Series.

1:2:6:8-*Tetranitronaphthalene.*—Five grams of 1:8-dinitronaphthalene were dissolved in a mixture of 25 c.c. of concentrated sulphuric acid and 25 c.c. of nitric acid (D 1·5). The solution was kept over the steam-bath for about four hours, when about 2 grams of a white powder were obtained. The substance does not melt up to 300° (Found: N = 18·20. $C_{10}H_4O_8N_2$ requires N = 18·18 per cent.).

From the filtrate about 2 grams of 1:3:6:8-tetranitronaphthalene were obtained, which was purified by crystallisation from nitric acid.

Trinitro-β-naphthoic Acid.—Two grams of β-naphthoic acid were dissolved in 40 c.c. of concentrated sulphuric acid, and 25 c.c. of nitric acid (D 1·42) were added to the solution. On keeping the solution overnight, needles melting at 220° separated (Found: N = 13·58. $C_{11}H_5O_8N_3$ requires N = 13·68 per cent.).

From the filtrate another *trinitro*-compound, much in excess of the first, was obtained as a yellow precipitate on the addition of water. It melted and decomposed at 215° (Found: N = 13·47. $C_{11}H_5O_8N_3$ requires N = 13·68 per cent.).

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CXII.—*The Action of the Grignard Reagent on Aromatic Nitro-compounds.*

By HARRY HEPWORTH.

THE reaction between nitro-compounds and the Grignard reagent does not appear to have been the subject of many investigations. The earliest communication is that of Moureu (*Compt. rend.*, 1901, **132**, 837), who obtained ββ-diethylhydroxylamine by the action of magnesium ethyl iodide on amyl nitrite and nitroethane,

and a product, which was probably $\beta\beta$-dimethylhydroxyamine, by the action of magnesium methyl iodide on methyl nitrate.

Iocitsch (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 555) studied the action of magnesium phenylacetylene bromide on nitrobenzene in ethereal solution, and found that a crystalline compound was formed which, when decomposed with water, yielded a hydrocarbon, $C_{16}H_{10}$ (m. p. 87—88·5°). The constitution of this hydrocarbon was not further investigated.

Oddo (*Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 220) was the first to study the action of the Grignard reagent on any aromatic nitro-compounds in detail. His investigation was confined to a study of the action of magnesium ethyl iodide on nitrobenzene. It was found that when this was cautiously added to a well-cooled ethereal solution of magnesium ethyl iodide, a yellow compound, O:NPhEt·O·MgI, was precipitated, but on the addition of a further quantity of nitrobenzene, the precipitate suddenly became dark brown. The yellow compound gave with pyridine an additive compound, $C_8H_{10}O_2NMgI,C_5H_5N$, and also, when decomposed with water, gave rise to ethylaniline and a product, which Oddo describes as a red, uncrystallisable oil, with an odour suggestive of almonds. Beyond the separation of this oil into three fractions, it was not further investigated.

Bewad (*Ber.*, 1907, **40**, 3065) studied the action of magnesium or zinc alkyl iodides on esters of nitrous acid and on nitro-paraffins. It was found that in the preparation of β-dialkylhydroxylamines, the zinc alkyl usually employed can be replaced advantageously by zinc alkyl iodides or magnesium alkyl iodides when the esters of nitrous acid are used, but not in the case of nitro-paraffins. With the latter, the reaction follows two courses, in both cases the final product being a β-dialkylhydroxylamine, the one containing one alkyl group derived from the magnesium alkyl haloid employed, the other containing two.

In a short note (P., 1907, **23**, 153), Pickard and Kenyon described the results of some preliminary experiments on the action of *p*-nitrotoluene on magnesium alkyl haloids in ethereal solution. It is stated that *p*-nitrotoluene reacts very vigorously with organo-magnesium haloids in ethereal solution, thus forming an indefinite, amorphous, yellow compound, which, when treated with acids, yields principally *p*-nitrosotoluene, *p*-tolylhydroxylamine, 4:4′-azoxytoluene (probably by the interaction of the two former compounds), and *p*-toluidine.

It will thus be seen that comparatively little work has been carried out on the behaviour of the Grignard reagent with nitro-compounds, and it was decided to investigate the action of mag-

nesium methyl iodide and magnesium ethyl bromide on the simple mononitro-aromatic compounds, nitrobenzene, *o*- and *p*-nitrotoluenes, and α-nitronaphthalene. In these experiments, the Grignard compound was not prepared separately, but a mixture of nitro-compound and alkyl haloid, diluted with ether, was added drop by drop to well-cooled ether containing magnesium powder, the rate of addition of magnesium powder being such as to keep the magnesium in excess throughout the reaction. This method was first employed by Kipping and Davies (T., 1911, **99**, 296), and has been found by the author to be convenient in certain reactions where selective action of the Grignard compound is aimed at (T., 1919, **115**, 1203).

In this way, it was found that the rate of reaction between the nitro-compounds and the Grignard reagents could be controlled fairly easily, provided that the flask in which the reaction is carried out is cooled in ice.

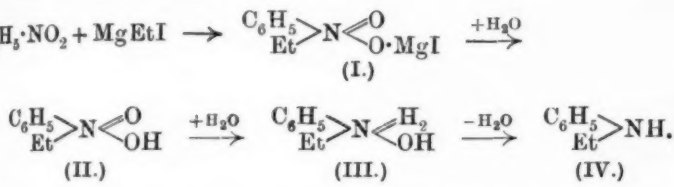
With nitrobenzene and magnesium methyl iodide or magnesium ethyl bromide, the existence of compounds corresponding with Oddo's compound, O:NPhEt·O·MgI (*loc. cit.*), has been confirmed. These compounds are pale yellow, and are best formed when the ratio of nitro-compound to magnesium alkyl haloid is about 2:3. On keeping for a few hours, these compounds become dark brown, especially if the temperature is allowed to rise. On decomposing the yellow additive compound with water, ethylaniline and azobenzene, together with unchanged nitrobenzene, were found to be the principal products of reaction. Magnesium methyl iodide reacted rather more energetically with nitrobenzene, with the production of methylaniline and azobenzene.

In a similar manner, it was found that magnesium ethyl bromide reacted with *p*-nitrotoluene, with the production of ethyl-*p*-toluidine and 4:4′-azotoluene, whilst magnesium methyl iodide gave rise to methyl-*p*-toluidine and 4:4′-azotoluene. With *o*-nitrotoluene, the analogous *o*-derivatives were formed. Under the conditions of the experiments, the formation of nitroso-compounds, hydroxylamine derivatives, and azoxy-compounds was not observed.

Finally, a few experiments were carried out with α-nitronaphthalene, from which moderate quantities of methyl- and ethyl-α-naphthylamines were obtained, whilst small quantities of αα′-azonaphthalene were also isolated.

Oddo (*loc. cit.*) has already suggested a possible mode of reaction to account for the formation of ethylaniline from nitrobenzene, and a similar view may be propounded to account for the production of bases from the other compounds studied by the

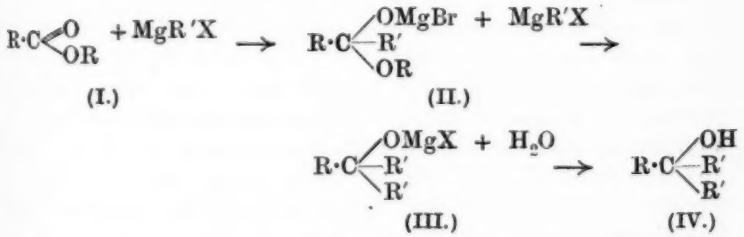
present author. According to Oddo, the primary reaction may be written as follows:



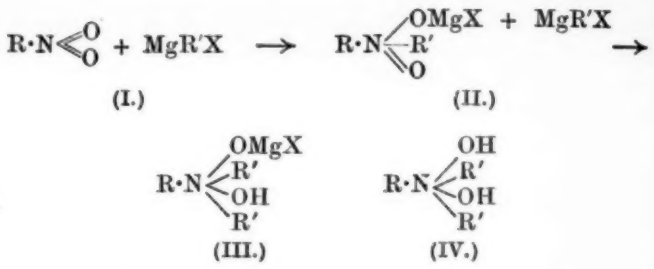
The experimental evidence which Oddo brings forward, and has now been confirmed, certainly justifies the formulation of compound I, but the formation of ethylaniline (IV) by the intermediate formation of III is open to question. There seems to be no objection to postulating that compound II loses oxygen directly with the formation of ethylaniline (IV). No compound analogous to II is known, so that it is impossible to speak with any degree of certainty as to its behaviour. At the same time, the loss of oxygen from such a compound is no more remarkable than the loss of carbon dioxide in the conversion of a simple monocarboxylic acid into the corresponding hydrocarbon, the more so if one accepts, what is probably the case, that compound II is very unstable and just as likely to lose oxygen as compound III is to lose water. In either case, compound II must lose oxygen prior to its conversion into ethylaniline.

The production of the other secondary bases may be accounted for in an analogous manner.

It is now necessary to account for the formation of azo-compounds without postulating the formation of nitroso-compounds or hydroxylamine derivatives during the course of the reaction. In this connexion, it is interesting to compare the action of excess of Grignard reagent with the esters of the simpler carboxylic acids and with the aromatic nitro-compounds. In the former case, the course of the reaction is as follows:



In the case of the aromatic nitro-compounds, the reaction may be represented as follows:



(I.) (II.)

(III.) (IV.)

Two molecules of III may be condensed, with the primary production of one molecule of an azo-compound and four molecules of Mg(OR)Br, or, on the addition of water, a compound of the type IV may be momentarily formed, two molecules of which lose four molecules of alcohol to give an azo-compound. At the same time, the intermediate formation of a compound such as the latter would be expected to give rise eventually to a dialkylaniline oxide.

In this connexion, it is interesting to note that azobenzene has also been prepared by Wieland and Roseeu (*Ber.*, 1912, **48**, 494) by the action of excess of magnesium phenyl bromide on nitrosobenzene, for which no explanation as to the mechanism of the reaction is given.

Experimental.

About 2 grams of magnesium powder and 5 grams of ethyl bromide, together with 200 c.c. of dry ether, were placed in a large flask provided with a stirrer, a reflux condenser, and a small, wide glass tube for the introduction of magnesium, and the reaction was started by introducing a little magnesium ethyl bromide prepared in a test-tube.

When the reaction was proceeding satisfactorily, the flask was surrounded by a mixture of ice and salt, and 123 grams (1 mol.) of freshly distilled nitrobenzene, 170 grams of ethyl bromide (1½ mols.), and 300 c.c. of dry ether were now added drop by drop to the well-stirred mixture, the whole addition taking about four and a-half hours. Forty grams (1½ mols.) of magnesium powder were introduced a little at a time in such a way as to ensure the presence of excess of magnesium throughout the reaction. The addition of each drop of the ethereal solution of ethyl bromide and nitrobenzene produced a hissing sound and a yellow precipitate. Towards the end of the addition the reaction became less vigorous.

A small quantity of the yellow precipitate was withdrawn, filtered, and quickly freed from any adhering magnesium powder.

After washing with a little ice-cold ether, a portion of the precipitate was converted into the pyridine double compound by boiling with pyridine under reflux for six hours, as described by Oddo (*loc. cit.*) (Found: Mg=7·31; N=8·30. Calc.: Mg=7·27; N=8·36 per cent.).

After remaining overnight, the contents of the flask had become dark brown. Sufficient water was added drop by drop to the well-cooled mixture, and the reaction vessel was warmed in order to remove a large portion of the product, which had adhered firmly to the walls.

The product was then extracted six to seven times with ether, the clear separation of the ethereal layer being accelerated in a centrifuge. The aqueous portion did not then contain more than traces of organic matter. After drying the ethereal layer, the ether was evaporated to 200 c.c., and then thoroughly extracted several times with aqueous oxalic acid in order to remove the bases present.

Ethereal Solution Free from Base.—The ethereal solution was dried, and, after removal of the ether, distilled under 15 mm. pressure. Six fractions were collected, as follows:

I.	115—123°, 22 grams	IV.	146—165°, 14 grams
II.	123—130°, 14 „	V.	168—175°, 7 „
III.	130—144°, 8 „	VI.	175—195°, 12 „

Above 195°, decomposition occurred, and the distillation was stopped. The residue in the flask weighed 8 grams. All these fractions were red. Fractions IV, V, and VI readily solidified in ice, whilst fraction III solidified on keeping in ice for twenty-four hours. These were transferred to a porous plate, and a red solid (m. p. 61—64°) was obtained. On recrystallisation from 90 per cent. alcohol, 27 grams of a substance crystallising in large red plates (m. p. 68·5°) were obtained. The identity of this product with azobenzene was established by its conversion into hydrazobenzene and benzidine. Thirty-four grams of unchanged nitrobenzene (b. p. 207°) were recovered on refractionating fractions I and II.

Oxalic Acid Extract.—Preliminary experiments had indicated that no hydroxylamine derivative was present in the acid extract. As this solution appeared to contain traces of impurities not extractable by ether, it was distilled in a current of steam for one hour. Traces only of a brownish-red oil passed over. The residue was rendered alkaline and the steam distillation continued until no more oil passed over. The oil was extracted with ether, dried, and, after removal of the ether, dried in a vacuum over solid

potassium hydroxide and paraffin wax. Twenty-five grams of an oil with an odour like that of aniline and a faint brown colour were obtained.

This oil distilled at 205—208°/762 mm., and was identified as ethylaniline. A sample submitted to analysis by the *R*-salt and acetic anhydride method did not show more than traces of primary or tertiary bases. A freshly distilled sample (b. p. 206—206·5°) was converted into the platinichloride (Found: Pt=30·0. Calc.: Pt=29·9 per cent.).

Action of Magnesium Methyl Iodide on Nitrobenzene.

This was carried out on similar lines to the previous experiment, 62 grams of nitrobenzene, 106 grams (1½ mols.) of methyl iodide, and 19 grams (1½ mols.) of magnesium powder being employed. The reaction was rather more vigorous, and yielded 22 grams of unchanged nitrobenzene, 15 grams of methylaniline, and 17 grams of azobenzene. In a further experiment, an attempt was made to separate the azobenzene and methylaniline from the dark product, obtained on decomposing the Grignard compound with water, by distillation in a current of steam. This was found to be extremely slow, and even after twelve hours' continuous distillation azobenzene continued to pass over. In subsequent experiments, the original method of separating the base by means of aqueous oxalic acid was reverted to, the residue being thoroughly dried and then distilled in a vacuum. The identity of the base with methylaniline was established by analysis of the platinichloride (Found: Pt=31·10. Calc.: Pt=31·24 per cent.).

Action of Magnesium Ethyl Bromide and Magnesium Methyl Iodide on p-*Nitrotoluene.*

A mixture of 40 grams of *p*-nitrotoluene, 70 grams (2 mols.) of ethyl bromide, and 150 c.c. of dry ether was added during three hours to 16 grams (2 mols.) of magnesium powder and 200 c.c. of ether, as in the previous experiments. At first a yellow precipitate was formed, but this was very transient, and the mixture quickly became brown.

The base was separated as before. On rendering alkaline and continuing distillation, a base (b. p. 216—219°) was collected. On redistillation, 9 grams of an oil (b. p. 216—217°) were obtained, which was identified as ethyl-*p*-toluidine (Found: N=10·56. Calc.: N=10·4 per cent. In platinichloride: Found: Pt=29·0. Calc.: Pt=28·7 per cent.).

The residue left from the extraction of the base was dried and distilled under 20 mm. pressure.

Three fractions were obtained.

Fraction 1,	110—135°,	5 grams
„ 2,	140—160°,	5 „
„ 3,	185—200°,	16 „

On working up fractions 2 and 3 as before, 17 grams of crude 4:4′-azotoluene were obtained, which, on recrystallisation from alcohol containing a little light petroleum, separated in long, yellow needles melting at 143·6° (Found: N=13·28. Calc.: N=13·37 per cent.). A mixture with an equal quantity of pure 4:4′-azotoluene melted at 144°.

In a similar experiment, in which 93 grams of methyl iodide were used in place of 72 grams of ethyl bromide, 8 grams of methyl-*p*-toluidine (b. p. 208—209°) and 15 grams of 4:4′-azotoluene (m. p. 144°) were obtained.

The effect of increasing the amount of alkyl haloid and magnesium was investigated, the quantity being raised to four molecular proportions to one of *p*-nitrotoluene. It was found that rather more azo-compound and base were produced, but even in these experiments there was some unchanged *p*-nitrotoluene.

Action of Magnesium Ethyl Bromide and Magnesium Methyl Iodide on o-Nitrotoluene.

A mixture of 40 grams of *o*-nitrotoluene, 72 grams of ethyl bromide, and 16·5 grams of magnesium powder was allowed to react exactly as in the case of *p*-nitrotoluene when 8 grams of ethyl-*o*-toluidine (b. p. 204—206°) and 12 grams of 2:2′-azotoluene (m. p. 55·4°) were obtained.

In a similar experiment, using 40 grams of *o*-nitrotoluene, 95 grams of methyl iodide and 16·5 grams of magnesium powder, 9 grams of methyl-*o*-toluidine (b. p. 207—208°) and 11 grams of 2:2′-azotoluene were obtained.

Action of Magnesium Ethyl Bromide and Magnesium Methyl Iodide on α-Nitronaphthalene.

A mixture of 52 grams of α-nitronaphthalene, 50 grams of ethyl bromide, and 200 c.c. of dry ether was slowly added to 200 c.c. of dry ether, to which 11 grams of magnesium powder were added in small portions from time to time. The usual yellow precipitate was formed, which became brown on keeping overnight. After decomposition with water, a base was extracted with oxalic acid, as in the previous experiments.

On rendering the acid extract alkaline and distilling in a current of steam, 15 grams of an oily base (b. p. 298—301°/754 mm.) were obtained. On keeping, the base became much darker, and appeared brown by transmitted light and violet-blue by reflected light. It was further purified by dissolving in dry ether and precipitating the hydrochloride with dry hydrogen chloride. The base, liberated by aqueous potassium hydroxide, boiled at 187—189°/15 mm. The platinichloride was analysed (Found: Pt = 25·80. Calc.: Pt = 25·93 per cent.).

This base therefore appears to be ethyl-α-naphthylamine, and its liberation from its salts by means of alkalis confirms the experiments of Morgan and Micklethwait (T., 1907, **91**, 1516), who negatived the statement of Limpricht (*Annalen*, 1856, **99**, 117) and Schiff (*ibid.*, 1857, **101**, 90) that the salts of this base, on treatment with potassium hydroxide, yielded α-naphthylamine.

The residue, after removal of the base, could not be distilled without decomposition, even under diminished pressure. The separation of a little αα′-azonaphthalene was achieved by precipitating an ethereal solution of the residue with dry hydrogen chloride. This precipitation was repeated several times, when a dark brown solid was eventually obtained. From this material 3 grams of αα′-azonaphthalene were obtained by careful sublimation. The sublimate was obtained as yellow leaflets which, on rubbing, became yellowish-red. On recrystallising from acetic acid, the substance was obtained in green needles melting at 185—189° (Found: N = 10·10. Calc.: N = 9·96 per cent.).

One gram of this substance was converted into hydrazonaphthalene by treating with 1·5 grams of solid sodium hydroxide and 100 c.c. of alcohol, heating to boiling, and adding zinc dust until colourless. On filtering into dilute yellow ammonium sulphide solution, separating, drying, and recrystallising from benzene, a substance was obtained which, when mixed with hydrazonaphthalene, melted at 275—276°.

A similar experiment with methyl iodide gave 16 grams of methyl-α-naphthylamine (b. p. 293—295°) and a small yield of αα′-azonaphthalene.

The author is indebted to the Research Committee of Messrs. Nobel's Explosives Company, Limited, and particularly to Mr. Rintoul, for the facilities accorded him in carrying out this investigation.

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CXIII.—*The Electro-affinity of Aluminium. Part III. The Acidity and Constitution of Aluminic Acid.*

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THE investigations of Slade (*Zeitsch. Elektrochem.*, 1911, **17**, 261), Blum (*J. Amer. Chem. Soc.*, 1913, **35**, 1499; 1914, **36**, 2383), and Hildebrand (*ibid.*, 1913, **35**, 864) show that aluminium hydroxide possesses acidic properties. There are, however, several other methods by means of which the acidity of aluminic acid can be determined. Thus, stable solutions of ammonium aluminate investigated physico-chemically prove the acidic function of aluminium hydroxide most distinctly, and these results agree with those obtained from sodium aluminate solutions, which will be considered first.

I. *Electrometric Titration of Sodium Hydroxide Solutions with Aluminic Acid.*

(*a*) *Conductivity Measurements.*—To dilute solutions of sodium hydroxide, small amounts of metallic aluminium were added, and the gradual decrease of conductivity was observed. The solutions were prepared by the action of pure sodium amalgam on conductivity water and kept in hard-glass bottles, into which weighed quantities of aluminium were introduced. After dissolution, the aluminate solutions were transferred through air-tight joints into conductivity cells with blank platinum electrodes. Atmospheric carbon dioxide was excluded by means of soda-lime tubes.

The metal used contained Al = 98·2, Cu = 0·94, Fe = 0·63 per cent.

The results of the first set of measurements, carried out in a thermostat at 25·0°, are:

In 0·0422*N*-sodium hydroxide.

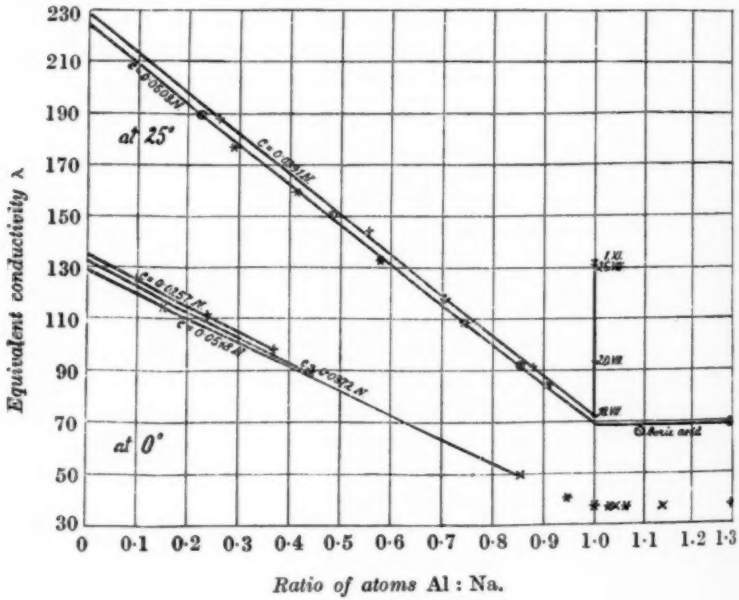
Gram-atoms of Al dissolved per litre.	Specific conductivity $K.10^3$.	$\lambda_{OH'}-\lambda_{Al'}=\frac{1000\Delta K}{\Delta C}$.
0	9·596	—
0·00314	9·124	150
0·00507	8·792	158
0·00778	8·380	158
0·00902	8·145	160
0·01209	7·706	156
0·01411	7·347	158

In 0·0257*N*-sodium hydroxide.

0	5·871	—
0·00259	5·463	157
0·00607	4·934	154
0·00943	4·338	162

The single solutions remained stable, showing no change in conductivity during many days. The difference of mobilities of the hydroxyl ion, $\lambda_{OH'}$, and the aluminate anion, $\lambda_{Al'}$, is calculated as $\frac{1000\,\Delta K}{\Delta C}$ where ΔC denotes the increase of aluminium in solution and ΔK the corresponding decrease of specific conductivity. The mean value, 158, gives $\lambda_{Al'} = 38$, $\lambda_{OH'}$ being taken as 196.

In the figure is shown the decrease of conductivity due to larger amounts of aluminium dissolved. The conductivity falls regularly with increasing concentration of aluminate, the slope remaining constant when the ratio of gram-atoms Al:Na is 1:3 or 1:2,



indicating that no formation of a salt of tri- or di-basic aluminic acid takes place. When, however, the ratio comes to 1:1, spontaneous decomposition of the solution occurs, during which crystalline aluminium hydroxide separates out, and the conductivity increases in the manner described by Slade and Polack (*Trans. Faraday Soc.*, 1914, **10**, 150).

In order to show that the decrease of conductivity effected by the dissolution of aluminium in alkali is not due to complex ionic "micelles," cryoscopic measurements were also carried out. To investigate how far the neutralisation of alkali by aluminic acid, the acidity of which might be questioned, differs from the action

of a recognised acid, such as boric acid, parallel experiments were made with the two acids.

The results, which are also plotted in the figure, were as follows:

In 0·05034*N*-sodium hydroxide.

Concentration of Al in gram-atoms.	Concentration of $B(OH)_3$ in gram-molecules.	Molec. cond. λ.		ΔT.		$i=\frac{\Delta T}{1\cdot86\,.\,C}$	
0	0	224·7		0·170°		1·82	
—	0·0112		189·6		0·175°		1·87
0·0144	—	177·0	—	0·176°	—	1·88	—
0·0206	—	159·0	—	0·183°	—	1·95	—
—	0·0243	—	150·9	—	0·176°	—	1·88
0·0296	—	132·3	—	0·186°	—	1·99	—
0·0375	—	108·2	—	0·179°	—	1·91	—
—	0·0430	—	92·8	—	0·180°	—	1·92
0·0459	—	84·5	—	0·174°	—	1·86	—
0·0503	—	79·7	—	0·179°	—	1·91	—
decomposes	0·0652	—	69·5	—	0·192°	—	2·05
—	0·0806	—	69·3	—	0·199°	—	2·12

The depression of freezing point, ΔT, first slightly increases, reaching a maximum for solutions half saturated with aluminium hydroxide. This indicates that a monobasic aluminate is formed, which is slightly more dissociated than the pure alkaline solution. The boric acid, being soluble, shows a continual increase in osmotic pressure, as evident from van't Hoff's coefficient, i; however, the changes in conductivity are in both cases identical.

To prevent the spontaneous decomposition of aluminates, it has been found necessary to work at 0°.

Since, however, the action of alkaline solutions on metallic aluminium ceases when the atomic ratio 1:1 is reached, amalgamated aluminium had to be added, in order to bring some more aluminium hydroxide in the nascent state into the solution. The amalgamation was effected by immersion in a solution of mercuric chloride; the amalgamated foil was then thoroughly rinsed with distilled water and introduced into the solution, which was kept in ice. At this temperature, the solutions were stable even when containing an excess of aluminium hydroxide. The conductivity of saturated 0·0257*N*- and 0·0372*N*-sodium hydroxide solutions was 36·8, and remained constant; only very slow increase could be observed when crystalline aluminium hydroxide was added.

The results are plotted in the figure. From the decrease of conductivity, again, the ionic mobilities at 0° were calculated; the mean difference of $\lambda_{OH'}-\lambda_{Al'}$ is 104, which gives $\lambda_{Al'}=14$, when $\lambda_{OH'}$ is taken as 117·7 (Kohlrausch, *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1026).

The important observation at 0°, namely, that the conductivity of aluminate solutions remains constant when the atomic ratio of Al:Na increases above 1:1, shows that there exists a definite saturation of one hydroxyl ion by one molecule of aluminium hydroxide, just as in the case of boric acid or (according to Kohlrausch, *Zeitsch. physikal. Chem.*, 1893, **12**, 782) of silicic acid. Judging from the phenomenon of spontaneous hydrolysis, during which aluminium hydroxide separates out, the action between the hydroxyl ion and the molecule may be regarded as addition rather than as neutralisation of the few hydrions due to the very sparingly soluble ortho-aluminic acid. The formation of meta-aluminic acid, AlO_2H, in solution cannot be expected, since the hydroxide, $Al(OH)_3$, does not lose water below 130°.

(*b*) *Measurements of Electromotive Force.*—The decrease of hydrion concentration effected by the addition of alkali to solutions of aluminium salts has been measured by Blum and Hildebrand (*loc. cit.*) by means of the potential of a hydrogen electrode. However, owing to the presence of aluminium salt and crystalline hydroxide, these measurements cannot be used for an exact determination of acidity. The same is the case with the experiments recently described by Fricke (*Zeitsch. Elektrochem.*, 1920, **26**, 129), from which no definite conclusion can be drawn, owing to the presence of finely divided aluminium hydroxide formed on hydrolysis in most concentrated alkali aluminate solutions. In the following experiments, the indicator of the hydrion concentration was the mercuric oxide electrode. This electrode was filled with a solution of sodium hydroxide (according to Donnan and Allmand, T., 1911, **99**, 845), and was gradually neutralised by the addition of weighed quantities of aluminium. The electrodes and the solutions were kept at 25·0°. Single measurements were carried out in each case four to six days after the dissolution of the aluminium. The electrodes were measured against a normal calomel electrode, the diffusion potential being eliminated by a saturated solution of potassium chloride.

In this way, the results on p. 1017 were obtained at 25·0° for the cell. C_{Al} denotes the amount of gram-atoms of aluminium dissolved per litre; "*E* calculated" was obtained from the potential, −0·1774 volt, of the *N*-sodium hydroxide–mercuric oxide electrode by means of the formula

$$E = -0{\cdot}1774 - 0{\cdot}0591 \log_{10}[C_{NaOH} - C_{Al}].$$

It is the value which would be obtained if a strong acid in the amount C_{Al} were added. The first solution decomposed before saturation was reached. The measurements made with the second

Hg | (HgO solid) NaOH solution | saturated KCl | *N*-calomel electrode

with 0·05417*N*-NaOH.			with 0·0189*N*-NaOH.		
$C_{Al.}$	*E.M.F.* observed in volt.	*E* calculated.	$C_{Al.}$	*E.M.F.* observed in volt.	*E* calculated.
— Nov. 20th	−0·1022	−0·1029	— Nov. 29th	−0·0779	−0·0760
0·0144	−0·0973	−0·0950	0·00505	−0·0690	−0·0681
0·0183	−0·0920	−0·0923	0·0102	−0·0581	−0·0568
0·0284	−0·0851	−0·0840	0·0157	−0·0356	−0·0305
0·0397	−0·0703	−0·0694	0·0183	−0·0078	+0·010
0·0542 Dec. 20th	decomposed	—	0·020	+0·0136	—
Dec. 31st	−0·0720	—	0·022 Jan. 6th	+0·0155	—
Jan. 2nd	−0·0820	—	Jan. 7th	+0·0140	
„ 6th	−0·0865	—	Jan. 8th	decomposed	—
„ 7th	−0·0870	—	—	—	—
„ 11th	−0·0862	—	—	—	—
„ 14th	−0·0857	—	—	—	—

solution, however, show that the solubility product of aluminic acid has been reached, since no appreciable change of potential took place when the number of aluminium atoms in solution exceeded that of sodium atoms.

The solubility product of aluminic acid is therefore

$$K_a = [\mathrm{Al'}] . [\mathrm{H^{\cdot}}] = \frac{C_{\mathrm{NaOH}} . K_w}{[\mathrm{OH'}]},$$

where K_w denotes the ionic product of water and C_{NaOH} the concentration of the sodium hydroxide solution, which for complete saturation becomes equal to the concentration of aluminic acid anions, denoted by [Al′].

Thus

$$0{\cdot}0591 \log_{10} \frac{C_{\mathrm{NaOH}}}{[\mathrm{OH'}]} = 0{\cdot}015 + 0{\cdot}0779 = 0{\cdot}093 \text{ volt.}$$

$$\frac{C_{\mathrm{NaOH}}}{[\mathrm{OH'}]} = \frac{[\mathrm{Al'}]}{[\mathrm{OH'}]} = 37{\cdot}3,$$

hence $K_a = 37{\cdot}3 \times 10^{-14}$ at 25·0°.

Similarly, the value of the solubility product of aluminic acid after spontaneous hydrolysis can be obtained from measurements of the first solution,

$$0{\cdot}0591 \log_{10} \frac{C_{\mathrm{OH'}}}{[\mathrm{OH'}]} = -0{\cdot}087 + 0{\cdot}102 = +0{\cdot}015 \text{ volt,}$$

$$\frac{C_{\mathrm{OH'}}}{[\mathrm{OH'}]} = 1{\cdot}795,$$

where $C_{\mathrm{OH'}}$ denotes the concentration of hydroxyl ions in the pure sodium hydroxide solution, and is equal to $0{\cdot}054 \times 0{\cdot}90N$, this solution being ionised to the extent of 90 per cent.

Hence [OH′] = 0·0272. The concentration of the aluminate

anions, [Al′], is then equal to $0{\cdot}0542-0{\cdot}0272=0{\cdot}0270N$, from which it follows that the solubility product of aluminic acid in the presence of crystalline aluminium hydroxide is

$$K'_a = \frac{0{\cdot}0270}{0{\cdot}0272}.10^{-14} = 10^{-14}.*$$

From measurements of electromotive force, it is evident that alkali is neutralised by freshly formed aluminium hydroxide until the ratio of molecules becomes 1:1, and that this neutralisation proceeds almost quantitatively, so that only a very small part, if any, can be present as colloidal alumina.

II. *Ammonium Aluminate.*

The solubility of aluminium hydroxide in aqueous ammoniacal solutions is usually described as variable, depending on the time and way of precipitation. Thus Archibald and Habasian (*Trans. Roy. Soc. Canada*, 1918, **11**, 1) found analytically several hundreds per cent. of alumina in dilute ammoniacal solutions, whereas Renz (*Ber.*, 1903, **36**, 2751) obtained higher solubility in precipitating solutions of barium aluminate with ammonium sulphate. If, however, amalgamated aluminium is dissolved in ammonia, regular and well-defined neutralisation takes place, and still higher solubility is reached, as is evident from the following experiments, consisting of conductivity, cryoscopic, and analytical determinations.

Measurements at 25°.

An ammoniacal solution of concentration $C_{NH_3}=0{\cdot}117N$, prepared by distilling pure ammonia into conductivity water out of contact with the atmosphere, showed the specific conductivity $K=3{\cdot}900\times10^{-4}$ mho. After some amalgamated aluminium had dissolved in it, the conductivity increased to $K'=5{\cdot}029\times10^{-4}$, indicating that ammonium salt was formed, the concentration of which can be calculated as follows.

Knowing the equivalent mobility of aluminate anion, $\lambda_{Al'}=38$, further $\lambda_{OH'}=196$ and $\lambda_{NH_4}=70{\cdot}4$, we have

$$1000\,K'=70{\cdot}4[NH_4^{\cdot}]+196[OH']+38[Al'].$$

Since, further,

$$[NH_4^{\cdot}]=[OH']+[Al'] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$1000\,K'=108{\cdot}4[NH_4^{\cdot}]+158[OH'].$$

* Slade (*loc. cit.*) previously found the solubility product of the dried crystalline hydroxide to be $0{\cdot}37\times10^{-14}$ at 25°.

According to the law of mass action, which holds in the case of ammonia,

$$C_{NH_3} \cdot k = [NH_4^{\cdot}] \cdot [OH'] = \left(\frac{1000\,K}{\lambda_{NH_4^{\cdot}} + \lambda_{OH'}}\right)^2 = \frac{(1000\,K)^2}{266^2} \quad . \quad . \quad (2)$$

From the last two equations we obtain

$$[NH_4^{\cdot}] = \frac{1000K' + \sqrt{(1000K')^2 - 4 \times 158 \times 108{\cdot}4 \times (1000K)^2 . 1/266^2}}{2 \times 108{\cdot}4}$$

as well as expressions for $[OH']$ and $[Al']$.

The observed values of K and K' given above lead to $[NH_4^{\cdot}] = 0{\cdot}00281N$ and $[Al'] = 0{\cdot}00155$ gram-molecule of aluminium hydroxide per litre.

Simultaneously, the increase of osmotic pressure, due to the formation of ammonium salt, has been determined by the lowering of freezing point of the ammoniacal solution, and was found to be $0{\cdot}226 \pm 0{\cdot}001°$, against $0{\cdot}220°$ of the pure solution. This change corresponds with an increase in concentration from $0{\cdot}118N$ to $0{\cdot}121N$, agreeing with the conductivity results, from which the sum of the concentrations of molecules and ions is 0·118 for the pure solution and 0·120 for the solution containing aluminium hydroxide.

Further, fresh quantities of amalgamated aluminium were added to this solution, and readings were continued until the conductivity ceased to rise. The following results were obtained:

$C_{Al'}$ concentration of Al added.	K specific conductivity observed.	$[Al']$ calculated.	$[NH_4^{\cdot}]$ calculated.	ΔT observed.	$\frac{\Delta T}{1{\cdot}86}$	$C_{NH_3} + [NH_4^{\cdot}]$.
—	$3{\cdot}900 \times 10^{-4}$	—	0·00146	0·220°	0·118	0·118
0·0040	5·029 ,,	0·00155	0·00281	0·226°	0·121	0·120
0·0060	6·662 ,,	0·00520	0·00559	0·229°	0·123	0·123
0·0088	9·594 ,,	0·00823	0·00848	0·231°	0·124	0·125
0·0129	9·45 ,,	—	—	0·228°	—	—
0·016	9·2 ,,	—	—	—	—	—
decomposes	3·910 ,,	0·00117	0·00216	—	—	—

From the solutions saturated with aluminium hydroxide, the ratio $[Al']:[OH'] = \frac{0{\cdot}000823}{0{\cdot}000253}$, which gives the ionic product $[Al'] \cdot [H^{\cdot}] = 32{\cdot}5 \times 10^{-14}$. (From electromotive-force measurements, $37{\cdot}3 \times 10^{-14}$ was obtained.)

These solutions, however, were not stable; some hours after saturation has been reached, crystalline aluminium hydroxide separated out (consisting of microscopic crystals), and the conductivity fell to a value $K' = 3{\cdot}910 \times 10^{-4}$, which remained constant.

Calculations of the solubility product, K'_a, from this reading give $\frac{0{\cdot}00117}{0{\cdot}00099} \times 10^{-14} = 1{\cdot}18 \times 10^{-14}$. During this experiment, the walls of the cell and the electrodes were covered with the crystalline hydroxide. A fresh solution of pure ammonia in conductivity water ($C_{NH_3} = 0{\cdot}2237$, $K = 0{\cdot}5380 \times 10^{-3}$) was introduced into this cell and allowed to dissolve some of the crystalline hydroxide. After several days, the conductivity rose to $K' = 0{\cdot}5405 \times 10^{-3}$, and remained constant. Again from K and K' the solubility product of aluminic acid in the presence of crystalline hydroxide follows $K'_a = 1{\cdot}23 \times 10^{-14}$.

In order to determine analytically the amount of aluminium hydroxide which remains in the solution after the spontaneous hydrolysis, the saturated ammoniacal solutions were allowed to decompose at 25·0° and kept in the thermostat for several days. After a week, the solutions were filtered (in absence of carbon dioxide) into a platinum dish and evaporated. The results were as follows:

C_{NH_3}.	Milligrams of Al_2O_3 in 100 grams of solution.	[Al'].	K'_a.
0·765*N*.	18·1, 19·3	0·00366	$1{\cdot}56 \times 10^{-14}$
0·523 „	14·6	0·00286	$1{\cdot}44 \times 10^{-14}$
0·160 „	7·2, 7·6	0·00145	$1{\cdot}27 \times 10^{-14}$

The constant K'_a was obtained in the following way.

From the equations (1), (2), and $\frac{[Al']}{[OH']} = K'_A$ it follows on elimination, that

$$[Al'] = \sqrt{\frac{k \cdot K'_a \cdot C_{NH_3}}{1 + K'_a}} = k' \sqrt{C_{NH_3}},$$

from which K'_a can be calculated. These values are, however, not quite constant, decreasing slightly with decreasing concentration.

Measurements at 0°.

Like the alkaline solutions of aluminium hydroxide, the ammoniacal solutions were also found to be quite stable at 0°. These solutions were prepared in the following way. To ammoniacal solutions carefully cooled in ice, amalgamated aluminium was added in a quantity sufficient to saturate the solution. The saturation was ascertained by conductivity readings, which first showed a steady increase, and after two days remained unchanged, although the dissolution of aluminium still proceeded.

TABLE I.

Concentration of ammonia. C_{NH_3}.	Observed conductivity of the pure solution. $K.10^3$.	Observed conductivity of saturated solution. $K'.10^3$.	Calculated from the values K and K'. $[NH_4^+]$.	$[OH']$.	$[Al']$.	$K_a=\frac{[Al']}{[OH']}\cdot K_w$	Mg. of Al_2O_3 in 100 grams of solution.	Mg. of Al_2O_3 in 100 grams of solution analytically determined.
0·4117	0·3670	1·052	0·0192	0·000285	0·0189	66·3 × K_w.	96·6	106, 103
0·2237	0·2835	0·7894	0·0144	0·000227	0·0141	62·4 „	72·2	73·1, 73·1
0·1592	0·2270	0·6773	0·01238	0·000169	0·0122	72·4 „	62·4	62·7, 62·4
0·1028	0·1866	0·5519	0·01008	0·00016	0·00992	71·5 „	—	—
0·0601	0·1467	0·3692	0·00668	0·000131	0·00655	50·4 „	—	—
0·0444	0·1292	0·3272	0·00592	0·000114	0·00580	50·9 „	29·6	25·8, 25·7
0·0300	0·1037	0·2670	0·00486	0·000746	0·00479	64·2 „	—	—
0·0283	0·1002	0·2534	0·00458	0·000089	0·00449	50·5 „	25·8	20·4, 20·1
0·00060	0·0265	0·0272	—	—	—	—	—	0·8, 1·5
0_* conductivity water	0·0020	0·0010	—	—	—	—	—	0·2, 0·1

Several days after the constant conductivity was attained, the solutions were filtered and analysed. The results are given in table I (p. 1021).

In solutions above $0{\cdot}5N$ there was a too vigorous evolution of hydrogen, which carried off some ammonia and caused less solubility. Below $0{\cdot}5N$, however, the solutions showed great constancy. The mobilities of the ions $NH_4^{\cdot}$ and OH' were taken as 39·3 and 117·7 respectively (Kohlrausch, *loc. cit.*), and the mobility of the aluminate ion, $\lambda_{Al'}$, as 14.

The solutions could be easily filtered. That no colloidal hydroxide passed through the filter is evident from experiments with conductivity water, in which amalgamated aluminium was allowed to dissolve for several days, and which consequently contained much of the hydroxide, yet after filtration and evaporation left no measurable residue. The formation of aluminium hydroxide in pure water causes a decrease in conductivity.

The last two columns of table I show the close agreement between the conductivity and analytical results. The rather less solubility observed in more dilute solutions is probably due to minute quantities of carbon dioxide in conductivity water.

Some freezing-point determinations were also carried out, for example:

C_{NH_3}.	$[NH_4^{\cdot}]$.	ΔT.	$\Delta T'$.	$\frac{\Delta T'}{1{\cdot}86}$.
$0{\cdot}1028N$	0·0101	0·189°	0·210°	0·113
$0{\cdot}0601N$	0·0067	0·109°	0·120°	0·065

where ΔT and $\Delta T'$ denote the depression before and after the dissolution of aluminium. It will be observed that the concentration calculated from the depression $\Delta T'$ (last column) is equal to the sum of molecules and ions, $C_{NH_3} + [NH_4^{\cdot}]$, exerting the osmotic pressure. It is evident that no complex compounds of ammonia and aluminium hydroxide are formed, since the amount which exists in solution never exceeds that theoretically required for neutralisation.

The freshly formed aluminium hydroxide microscopically examined appears granular and shows the metallic structure of aluminium.

III. *The Constitution of Aluminic Acid.*

In the experiments described above it is shown that at the ordinary temperature sudden change in aluminate solutions occurs, during which a large part of the dissolved aluminium hydroxide separates out in crystalline form, the ratio $[Al']:[OH']$ reaching after considerable time the value 1·5—1·1. Similar values can

be obtained from final conductivities acquired after the spontaneous decomposition, assuming that the aluminate ion is the same as in solutions before the decomposition.

Thus at 25° in 0·0391*N*-sodium hydroxide, four months after the decomposition, the final molecular conductivity, $\lambda=133{\cdot}1$, was observed; this is the conductivity of 0·0391*N*-sodium hydroxide when containing aluminium hydroxide dissolved in the ratio $[Al']:[OH']=1{\cdot}5$ before the decomposition. Hence

$$K'_a=1{\cdot}5\times10^{-14}.$$

Similarly, from 0·0422*N*-sodium hydroxide, after one month, $\lambda=116{\cdot}6$, $K'_a=1{\cdot}8\times10^{-14}$, and from 0·0257*N*-sodium hydroxide, after three weeks, $\lambda=125{\cdot}9$, $K'_a=1{\cdot}7\times10^{-14}$. Physical properties as well as analytical composition of solutions before the decomposition, were found identical with the properties of solutions of equal conductivity after the decomposition.

The supersaturation phenomena suggest that the compound formed by interaction between one molecule each of sodium hydroxide and aluminium hydroxide is the additive compound, $NaOH,Al(OH)_3$, which can be regarded as the sodium salt of aquo-aluminic acid, $H'[Al(OH)_4]'$, as suggested by Pfeiffer (*Ber.*, 1907, **40**, 4036). The process in the solution is therefore the following one: the hydroxyl ion joins the freshly precipitated molecule of aluminium hydroxide, and forms the anion of the aquo-aluminic acid, thus:

$$Al(OH)_3+OH' \rightleftharpoons Al(OH)_4'.$$

The anions, $Al(OH)_4'$, joining hydrions form partly the very sparingly soluble acid, $HAl(OH)_4$, the ionic product of which is $7{\cdot}7\times10^{-14}$ at 0°* and 35×10^{-14} at 25°. (From these two constants, the heat of electrolytic dissociation of aquo-aluminic acid, calculated by means of van't Hoff's isochore, is 4900 cal.) In time, some of the aquo-aluminic acid decomposes by heat or traces of carbon dioxide, forming the ortho-hydroxide, the particles of which grow until they reach such an insolubility that the constant K_a of the aquo-aluminic acid becomes too large for the mass action of the above equation, according to which $[Al(OH)_3]=k\,.\,K_a$.

Consequently, the above reaction must proceed in the reverse direction until all solid aquo-aluminic acid disappears, which causes the sudden growth of crystals of aluminium hydroxide and extensive hydrolysis of the solution.

It was observed that the addition of crystalline hydroxide to a solution of aluminate also causes spontaneous hydrolysis.

* According to Noyes' numbers (*Zeitsch. Physikal. Chem.*, 1910, **73**, 1), K_w at 0° is 0·11 K_w at 25°.

At higher temperatures, the two solid phases, namely, the aquo-aluminic acid and aluminium hydroxide, cannot co-exist, but at 0° their transition temperature seems to be reached.

The crystalline aluminates furnish further evidence for the aquo-aluminates, which are fully hydrated (Werner, "Neuere Anschauungen," 1920, 4th ed., p. 126), and lose water in the same manner as aluminium hydroxide itself (Beckmann, *J. pr. Chem.*, 1882, [ii], **26**, 385). Hydroxylic groups, which, according to Hantzsch's researches (*Ber.*, 1917, **50**, 1422), never split off an acidic hydrion, are all only basic in aluminium hydroxide. The acidity of this compound consists in the formation of additive compounds with alkalis.

The close resemblance of boric and aluminic acids (see figure) suggests that boric acid also forms aquo-salts, which is seen most markedly in the cases of borax, $Na_2B_4O_7,10H_2O$, and lithium aluminate, $Li_2Al_4O_7,11H_2O$ (Allen and Rogers, *Amer. Chem. J.*, 1900, **24**, 304), which are analogous aquo-salts of the type $M^{I}OH{\cdot}M^{III}(OH)_3 + HOH{\cdot}M^{III}(OH)_3$.

Appendix.

In this and in a previous paper (this vol. p. 11) the basigenic and acidigenic character of aluminium has been investigated from the point of view of the ionic splitting of its compounds in aqueous solutions. According to Abegg's theory of electroaffinity, basic or acidic properties of the hydroxide should be in close connexion with the electrolytic potential of the metal. However, in the case of aluminium, a metal of high position in the electro-potential series (E.P. $= -1{\cdot}34$ volt, $H = 0$; compare this vol., p. 27), this forms a hydroxide of feebly basic properties (the ionic product of basic splitting is 10^{-33}; compare this vol., p. 20), and at the same time of distinctly acidic character. The chloride, on the other hand, is very soluble and largely ionised, resembling in this respect the alkali haloids.

Obviously, Abegg's idea, that the electrolytic potential might be a measure of basicity, is not quite sound. There are heavy metals of more positive potential, such as silver, thallium, and lead, the hydroxides of which are fairly strong bases, and light metals of more positive potential, for instance, aluminium and zinc, of feebly basic hydroxides.

It seems that, besides the electron affinity, which represents the case of escape of a valency electron from the atom, also the mass of the ion influences the basicity of the oxide and, in general, the ionisation of the compound. Thus Beketov's rule (*Phil. Mag.*,

1865, [iv], **31**, 306), according to which the stability of a compound is the greater the more equal are the equivalent weights of the components, might be extended for ionisation processes.

We may therefore expect that a compound will ionise the easier the greater the difference in polarity (in the electrolytic potential) of the constituting ions and the more unequal their masses. Aluminium hydroxide is least, fluoride more, chloride, bromide, iodide most of all, ionised.

The acidity seems to depend, however, in general on the equivalent volume of the oxide, in that a small equivalent volume is accompanied by acidic properties, provided the basicity is feeble. Thus the small equivalent volume of alumina (4·1, which, next to that of glucina, is the least of all oxides) is connected with the acidity, developed in spite of the high position of aluminium in the potential series.

Summary.

(1) Electrometric measurements show that aluminium hydroxide neutralises alkalis as a monobasic acid. The mobility of alumination is 38 at 25° and 14 at 0°.

(2) Stable solutions of ammonium aluminate were obtained, for which the law of mass action holds good.

(3) The ionic product of aluminic acid is 35×10^{-14} at 25° and $7{\cdot}7 \times 10^{-14}$ at 0°; in the presence of crystalline aluminium hydroxide it is $1{\cdot}5 \times 10^{-14}$ at 25°.

(4) Evidence is adduced that aluminates are additive compounds of the type $M^{\cdot}[Al(OH)_4]'$, that is, salts of aquo-aluminic acid, $H^{\cdot}[Al(OH)_4]'$.

(5) The relation existing between the basicity, acidity, and the electrolytic potential is discussed.

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CXIV.—*The Nature of the β-Ferricyanides and the β-Ferrocyanides.*

By Samuel Henry Clifford Briggs.

It was found by Bennett (T., 1917, **111**, 490) that the α- and the β-ferrocyanides (Briggs, T., 1911, **99**, 1019) are identical from a crystallographical point of view, and it therefore appeared probable that the β-ferrocyanides would prove to be mixtures of the ordinary ferrocyanides with a very small amount of highly-coloured impurity.

In view of Bennett's results, it was decided to make a further investigation of the two ferrocyanides, and also of the α- and β-ferricyanides of Locke and Edwards (*Amer. Chem. J.*, 1899, **21**, 193, 413; see also Bellucci and Sabatini, *Atti R. Accad. Linci*, 1911, [v], **20**, **1**; Piutti, *Ber.*, 1912, **45**, 1830; Hauser and Biesalski, *ibid.*, 3516; Wells, *Amer. Chem. J.*, 1913, **49**, 205). It is shown below that the β-ferricyanides are compounds of ferricyanide and aquopentacyanoferriate, whereas the β-ferrocyanides are mixed crystals of ferrocyanide and aquopentacyanoferroate, the amount of the latter being far too small to be detected by any known method of quantitative or qualitative analysis.

The β-Ferricyanides.

The analysis of the salt prepared according to the directions of Locke and Edwards pointed to the formula

$$3K_3Fe[Fe(CN)_6],K_2[Fe(CN)_5H_2O]$$

rather than to Locke and Edwards' formula, $K_3Fe(CN)_6,H_2O$, but as it was scarcely possible to determine the exact formula of the double salt by analysis, synthetical means were used for this purpose. A simple method for the preparation of potassium aquopentacyanoferriate could not be devised, however, and recourse was therefore had to the sodium salt, which can readily be obtained by Hofmann's method (*Annalen*, 1900, **312**, 1). It was found that a solution of this salt with three and a-half molecular equivalents of sodium ferricyanide was precipitated at once with bismuth nitrate, proving that free ferricyanide was present, whereas a solution containing two and a-half molecular equivalents of sodium ferricyanide did not give a precipitate after a week, and consequently did not contain free ferricyanide. The formula of sodium β-ferricyanide would therefore appear to be

$$3Na_3[Fe(CN)_6],Na_2[Fe(CN)_5H_2O].$$

The ferricyanides in solution appear to decompose to some extent, as shown by the equation

$$K_3[Fe(CN)_6] + H_2O \rightleftharpoons K_2[Fe(CN)_5H_2O] + KCN.$$

The potassium cyanide produced gives cyanide ions, and these are removed on addition of acids, owing to formation of the very slightly dissociated hydrogen cyanide. Acids therefore increase the velocity of the reaction towards the right. Alkalis and ammonia, on the other hand, decompose the aquopentacyanoferriate (compare Hofmann, *loc. cit.*), and cyanides convert the aquopentacyanoferriate into ferricyanide, thereby increasing the reaction towards the left.

These transformations are shown by the colour changes developed in solutions of potassium ferricyanide when the above-mentioned reagents are added, acids causing an intensification of colour, owing to increase of aquopentacyanoferriate, whereas alkalis, ammonia, and cyanides diminish the colour, owing to removal of the intensely coloured aquopentacyanoferriate.

When pure, bright orange-red potassium ferricyanide is recrystallised from a solution containing 2 or 3 per cent. of sodium aquopentacyanoferriate, garnet-red crystals are obtained, differing very much in habit from the orange-red crystals of the pure salt. These garnet-red crystals are analogous to potassium β-ferrocyanide, as shown below.

There is thus an explanation of the very deep colour of many preparations of potassium ferricyanide made by oxidising potassium ferrocyanide with chlorine, for not only does the chlorine oxidise the ferrocyanide, but it also decomposes the ferricyanide to some extent, according to the equation

$$K_3[Fe(CN)_6] + H_2O + Cl_2 = KCl + CNCl + K_2[Fe(CN)_5H_2O],$$

as found by Cambi (*Gazzetta*, 1911, **41**, i, 157). The deeply coloured crystals are therefore mixed crystals of potassium ferricyanide, and the double salt of ferricyanide and aquopentacyanoferriate (β-ferricyanide).

The Action of Bromine on Potassium Ferricyanide.

In view of the above-mentioned observations of Cambi, it appeared probable that the action of bromine on potassium ferricyanide would furnish a convenient method for the preparation of "β-ferricyanide," and this expectation was realised, further evidence thus being provided for the constitution suggested above. Larger quantities of bromine gave a brownish-black colloidal substance of the formula IX or X, whilst with excess of bromine,

greenish-black, insoluble ferric cyanide was formed (compare Reynolds, T., 1888, **53**, 769; Messner, *Zeitsch. anorg. Chem.*, 1895, **9**, 126). A small quantity of a white solid sparingly soluble in hot water was produced, together with the ferric cyanide. The analysis of this substance suggested a polymeride of cyanic acid, but the amount was too small for complete identification.

The Action of Hydrochloric Acid on Potassium Ferricyanide.

The action of hydrochloric acid on potassium ferricyanide (I) has been studied beyond the stage of the formation of Locke and Edwards' β-ferricyanide (V). Although the acid successively removes the three molecules of potassium cyanide, with the final production of ferric cyanide (IV), it has not been possible to isolate potassium aquopentacyanoferriate (II) or the hitherto unknown diaquotetracyanoferriate (III). Not only are the compounds II and III extremely soluble in water and difficult to isolate in the crystalline state, but the compounds I, II, III, and IV have a pronounced tendency to combine with each other, with or without elimination of water molecules, to give the substances V, VI, VII, and X.

$K_3[Fe(CN)_6]$ (I.) $\quad K_2\left[Fe\begin{matrix}(CN)_5\\H_2O\end{matrix}\right]$ (II.) $\quad K\left[Fe_2\begin{matrix}(CN)_4\\2H_2O\end{matrix}\right]$ (III.)

$Fe(CN)_3$ (IV.) $\quad 3K_3[Fe(CN)_6],K_2\left[\begin{matrix}Fe(CN)_5\\H_2O\end{matrix}\right]$ (V)

$K_2\left[Fe\begin{matrix}(CN)_5\\H_2O\end{matrix}\right],K\left[Fe_2\begin{matrix}(CN)_4\\2H_2O\end{matrix}\right]$ (VI.) $\quad 2K[Fe(CN)_4],Fe(CN)_3,H_2O$ (VII.)

$3K[Fe(CN)_4],2Fe(CN)_2,8H_2O$ (VIII.) $\quad 3K[Fe(CN)_4],K_2[Fe(CN)_5H_2O],H_2O$ (IX.)

$Fe(CN)_3,K[Fe(CN)_4],2K_2[Fe(CN)_5H_2O]$ (X.) $\quad \left[\begin{matrix}CN & CN & CN\ldots\\\ldots FeCN & FeCN & FeCN\ldots\\CN & CN & CN\ldots\end{matrix}\right]$ etc. (XI.)

Although the formulæ V—X are useful as showing the way in which the compounds are derived from potassium ferricyanide, it is probable that these substances are not simply double salts, but rather salts of highly complex anions containing several iron atoms and a correspondingly large number of cyanogen groups. Evidence for this view is obtained from the distinctive precipitation reactions of Locke and Edwards' salt, and also from the properties of

ferric cyanide, which is a highly insoluble salt with colloidal properties instead of a readily soluble substance, as would be expected from the simple formula IV. Ferric cyanide would therefore appear to be highly polymerised, possibly with each iron atom at the centre of a regular octahedron, a cyanogen group at each corner, and every cyanogen group united to at least two iron atoms. The simplest structure of this type is seen in the "chain" formula XI.

The β-Ferrocyanides.

Potassium β-ferrocyanide crystallises on cooling from a warm, saturated solution of the α-ferrocyanide containing one part of sodium aquopentacyanoferroate (compare Hofmann, *loc. cit.*) per hundred parts of the ferrocyanide. The β-ferrocyanides are therefore mixed crystals of ferrocyanide and aquopentacyanoferroate, the amount of the latter being far too small to be detected by qualitative or quantitative analysis.

Since potassium β-ferrocyanide is formed when the α-ferrocyanide is repeatedly recrystallised from water, it follows that the ferrocyanides in aqueous solution are in a state of equilibrium, as seen from the equation

$$H_2O + K_4[Fe(CN)_6] \rightleftharpoons K_3[Fe(CN)_5H_2O] + KCN.$$

The effect of acids, alkalis, ammonia, and cyanides on this equilibrium is analogous to that described above in the case of the ferricyanides, and need not be referred to in detail. It is sufficient to say that a simple explanation is hereby provided for the various transformations mentioned in the former paper (T., 1911, **99**, 1019).

The possibility that the β-ferrocyanides are α-ferrocyanides containing a trace of a highly-coloured impurity was considered in the former paper, but as two *l*-menthylammonium ferrocyanides were obtained which differed considerably in specific rotation, it was concluded that the α- and β-ferrocyanides were isomeric. The *l*-menthylammonium α-ferrocyanide has $[\alpha]_D^{17} - 42{\cdot}4°$ and the β-ferrocyanide $[\alpha]_D^{17} - 28{\cdot}5°$. Further, on adding a trace of acid to a solution of the α-ferrocyanide in alcohol, the specific rotation was observed to fall from $-40{\cdot}9°$ to $-31{\cdot}8°$.

The former preparation of *l*-menthylammonium β-ferrocyanide was no longer available, but there can be no doubt from its properties, as previously described, that it contained aquopentacyanoferroate as well as ferrocyanide. Whether its low rotatory power was due to some change of the nature of racemisation in the *l*-menthylammonium groups or to the presence of some impurity cannot now be decided, and this point remains obscure. An ex-

planation of the fall in rotation of the *l*-menthylammonium α-ferrocyanide on the addition of acid has been furnished by a study of quininium primary ferrocyanide. When the quininium salt was dissolved in alcohol or acetone, the specific rotation was found to rise for some days, and then become constant, the change being as much as 20° in some experiments. An examination of the product showed that ferricyanide was present, the salt having undergone oxidation by atmospheric oxygen dissolved in the solution. It was then observed that the preparation of *l*-menthylammonium ferrocyanide described in the former paper also underwent oxidation when its solution in alcohol was exposed to the air for some time, and from the residue pure *l*-menthylammonium ferricyanide was isolated.

This tendency of the ferrocyanides of substituted ammonium bases to undergo oxidation by atmospheric oxygen is probably the result of slight dissociation into base and acid, for example,

$$(C_{10}H_{19}\cdot NH_3)_4Fe(CN)_6 \rightleftharpoons 4C_{10}H_{19}\cdot NH_2 + H_4Fe(CN)_6.$$

The addition of acid will increase the amount of the readily oxidisable hydrogen ferrocyanide, and thereby accelerate the change. This will account for the fall in rotation previously observed on the addition of acid to an alcoholic solution of *l*-menthylammonium α-ferrocyanide. The solution used was dilute, and the amount of oxygen required to oxidise all the ferrocyanide present was very small, and would easily be provided by air dissolved in the liquid.

Experimental.

Locke and Edwards' Potassium β-Ferricyanide.

The salt prepared according to the directions of Locke and Edwards (*loc. cit.*) was obtained as a yellowish-green solid. Its precipitation reactions agreed exactly with the observations of Locke and Edwards, but the analysis was not in accordance with their formula, $K_3Fe(CN)_6.H_2O$. They decomposed their salt with nitric acid, and for this reason, apparently, their figures for the iron content were too low, as it was found impossible during the present research to obtain complete decomposition when using nitric acid. On heating the salt with concentrated sulphuric acid, however, the complex was entirely destroyed. On diluting the product with a little water and carefully neutralising with ammonia, the double salt of potassium and ferric sulphates, which is practically insoluble in the presence of acid, could be readily dissolved on warming, and the analysis carried out in the usual manner.

		K.	Fe.	N.	H_2O
$K_3Fe(CN)_6.H_2O$	requires	33·78	16·08	24·21	5·19
Found		33·82	17·61	24·73	0·83 (at 160°)
$3K_3Fe(CN)_6.K_2[Fe(CN)_5.H_2O]$	requires	33·87	17·59	25·37	1·42
$4K_3Fe(CN)_6.K_2[Fe(CN)_5.H_2O]$	,,	34·23	17·46	25·41	1·13
$5K_3Fe(CN)_6.K_2[Fe(CN)_5.H_2O]$	,,	34·47	17·37	25·43	0·93 per cent.

When heated to 210°, the salt underwent further decomposition, with loss of cyanogen. The analysis points to a compound of aquopentacyanoferriate and ferricyanide rather than to a salt of the formula $K_3Fe(CN)_6.H_2O$, but it is scarcely possible to determine the exact formula of the double salt by quantitative analysis alone. In agreement with the analytical data, it was found that the compound gave the characteristic reaction for iron pentacyano-derivatives described by Hofmann (*loc. cit.*), for when its solution was treated with hydroxylamine hydrochloride rendered alkaline with sodium hydroxide and heated, it became deep golden-yellow with copious effervescence.

An attempt was made to determine the constitution by titration with potassium cyanide until the colour of aquopentacyano-ferriate had disappeared, but no definite end-point was obtained, showing that potassium ferricyanide has a tendency to decompose in solution according to the equation

$$K_3Fe(CN)_6 + H_2O \rightleftharpoons K_2[Fe(CN)_5H_2O] + KCN.$$

During the titration of the β-ferricyanide with potassium cyanide, it was noted that the solution, on keeping, deposited a little Prussian-blue, in agreement with the observations of Hauser and Biesalski (*loc. cit.*).

The Action of Bromine on Potassium Ferricyanide.

Preparation of Locke and Edwards' Salt.—Ten grams of potassium ferricyanide were dissolved in 50 c.c. of water, and 1·4 grams of bromine were added to the cold solution. The mixture was kept in a stoppered bottle, the bottle being occasionally shaken. After three days, the solution no longer contained free ferricyanide, as shown by the absence of a precipitate with bismuth nitrate. On precipitating with 150 c.c. of alcohol (90 per cent.), the salt was obtained as a greenish-brown, crystalline dihydrate (Loss over sulphuric acid in a vacuum = 2·61. Calc.: 2·75 per cent.). Analysis of the dehydrated salt gave K = 34·04; Fe = 17·64; N = 24·86. $3K_3[Fe(CN)_6],K_2[Fe(CN)_5H_2O]$ requires K = 33·87; Fe = 17·59; N = 25·37 per cent. When prepared in this manner, the compound was free from Prussian-blue, and therefore gave a

yellowish-white precipitate with stannic chloride. The salt also gave Hofmann's reaction for iron pentacyano-compounds.

The Brownish-black Colloid,

$$Fe(CN)_3,K[Fe(CN)_4],2K_2[Fe(CN)_5H_2O].$$

—Eight grams of bromine were added to a solution of 12 grams of potassium ferricyanide in 60 c.c. of cold water, and the mixture was kept in a loosely stoppered bottle at the summer temperature (20—25°). Some gas was evolved, and the solution, after changing colour to brown and then to violet, deposited a black jelly. After ten days, the mixture was poured into 200 c.c. of alcohol (90 per cent.), and the black solid collected and dried in the air. It was then powdered and washed on a filter with cold water until free from soluble impurities. The compound now increased greatly in volume, owing to absorption of water, and the jelly-like mass which resulted was analysed after drying in a vacuum over sulphuric acid until its weight was constant (Found: K = 21·60; Fe = 24·08; N = 26·21. Calc.: K = 21·79; Fe = 24·90; N = 26·55 per cent.).

The compound was soluble in hydrochloric acid, with production of a characteristic, greenish-blue colour. It dissolved in warm water to a dark brown, colloidal solution.

The Action of Hydrochloric Acid on Potassium Ferricyanide.

The Bluish-violet Compound,

$$K_2[Fe(CN)_5H_2O],K[Fe(CN)_42H_2O].$$

—Ten grams of potassium ferricyanide dissolved in 20 c.c. of water were treated with 5 c.c. of hydrochloric acid (D 1·15) in an open flask immersed in water at 70—80° for forty minutes. The solution was allowed to remain overnight and filtered. The deep purple filtrate was then precipitated with two volumes of alcohol (90 per cent.). The semi-solid deposit was dissolved in a very small amount of water and precipitated with two volumes of alcohol, the process being repeated ten or twelve times until the alcoholic layer had a bluish-violet colour without any red or yellow tinge. The product was now dissolved in the smallest possible quantity of water, and a trace of Prussian-blue was removed by filtration. The filtrate was evaporated to dryness in a vacuum over sulphuric acid, leaving an extremely soluble, highly deliquescent, friable, black solid. Three and a-half grams were obtained from 35 grams of potassium ferricyanide (Found: K = 23·70; Fe = 21·69; N = 24·00. Calc.: K = 22·69; Fe = 21·59; N = 24·38 per cent.). At 160° one molecule of water was evolved, the loss in weight being 3·51 (Calc.: 3·48 per cent.).

The Greenish-black Compound, $2K[Fe(CN)_4],Fe(CN)_3,H_2O$.—

Twenty grams of potassium ferricyanide were dissolved in 40 c.c. of water, and 16 c.c. of hydrochloric acid (D 1·15) added. The mixture was heated at 55—60°, the solution being filtered every ten hours to remove the precipitated ferric cyanide. After the fourth filtration, only a small amount of ferric cyanide separated, and the acid reaction was very weak. The heating was continued a further twelve hours (fifty-two hours in all), and the cold solution was then precipitated with two volumes of alcohol (85 per cent.). The black, semi-solid deposit was purified by repeated solution in water and precipitation with alcohol (85 per cent.) at a room temperature of 20—25°, the quantities used being 15 c.c. of water and 30 c.c. of alcohol, once; 10 c.c. of water and 20 c.c. of alcohol, twice; 5 c.c. of water and 10 c.c. of alcohol, twice; and 5 c.c. of water and 15 c.c. of alcohol, three times. During the final stages of purification, the compound was obtained in the solid state, the yield of pure salt being half a gram. This was dissolved in a small quantity of water, evaporated to dryness over sulphuric acid, and weighed for analysis. On exposure for some weeks in a vacuum over sulphuric acid, it slowly evolved a molecule of water (Found: K = 14·67; Fe = 30·26; H_2O = 3·00. Calc.: K = 14·22; Fe = 30·47; H_2O = 3·28 per cent.). The compound was deliquescent and very readily soluble in water to a greenish-black solution.

The Dark Blue Compound, $3K[Fe(CN)_4],2Fe(CN)_2,8H_2O$.—Forty grams of potassium ferricyanide dissolved in 80 c.c. of water were heated at 55—60° with 12 c.c. of hydrochloric acid (D 1·15). A further 32 c.c. of hydrochloric acid were added in quantities of 8 c.c. at intervals of twelve hours, the heating being continued for twelve hours after the last portion of acid had been added, or sixty hours in all.

The filtrate from the dark green precipitate (*A*) was greenish-blue (volume, 100 c.c.). One hundred and fifty c.c. of alcohol (85 per cent.) were added, and the viscid deposit was dissolved in 15 c.c. of water and filtered. The magnificent deep blue solution was precipitated with 45 c.c. of alcohol (85 per cent.), and the treatment repeated a few times, 15 c.c. of water and 45 c.c. of alcohol being used on each occasion at a room temperature of 20—25°. The salt was finally obtained as a deep indigo-blue powder free from white crystals of potassium chloride. When exposed over sulphuric acid in a vacuum for three weeks, it lost four molecules of water, and the weight thereafter remained constant [Loss = 7·73. Calc.: 7·53 per cent. for a loss of $4H_2O$ from $3K[Fe(CN)_4],2Fe(CN)_2,8H_2O$. The residue then gave K = 13·19; Fe = 31·52; N = 25·96. $3K[Fe(CN)_4],2Fe(CN)_2,4H_2O$ requires K = 13·26; Fe = 31·55; N = 25·45 per cent.].

The green precipitate (*A*), after drying, had the composition

Fe:2·78N:0·05K:xH$_2$O. It therefore consisted of a slightly decomposed ferric cyanide, which salt was shown by Messner (*loc. cit.*) to lose cyanogen with great ease. This decomposition explains the presence of ferrous iron in the deep blue compound.

The compounds represented by the formulæ II to X are all intensely coloured.

Those compounds which had been subjected to prolonged treatment with alcohol in the course of purification gave an odour of *iso*cyanides when decomposed with alkalis. This reaction may be due to the presence of a trace of the corresponding ethyl esters, and is significant in view of the results of Bellucci and Sabatini (*loc. cit.*).

The compounds VI, VII, VIII, and X all give ferrocyanide as well as ferricyanide when decomposed by alkalis. It does not follow, however, that they all contain ferrous iron, since Messner has shown (*loc. cit.*) that compounds like cupric ferricyanide, $Cu_3[Fe(CN)_6]_2$, behave in the same way.

Quininium Primary Ferrocyanide.

Four grams of potassium ferrocyanide in 200 c.c. of water were added with stirring to a solution of 16 grams of quinine monohydrochloride in 400 c.c. of water in the cold. After two days, the pure, white icosahydrate was collected, washed with water, and dried in the air. On dehydration over sulphuric acid in a vacuum, it rapidly lost 17H$_2$O, and a further two molecules were evolved more slowly, the weight becoming constant after five weeks. The product was a hygroscopic, yellow monohydrate.

Analysis of the icosahydrate gave: Fe=3·08; H$_2$O=18·12, 18·11. $(C_{20}H_{25}O_2N_2)_4Fe(CN)_6,20H_2O$ requires Fe=2·98; 19H$_2$O=18·27. The monohydrate gave C=67·22, 67·46; H=6·38, 6·64; Fe=3·69, 3·75. Calc.: C=67·42; H=6·72; Fe=3·65 per cent.

Quininium secondary ferrocyanide,

$$(C_{20}H_{26}O_2N_2)_2Fe(CN)_6,22H_2O,$$

separated as a black solid, insoluble in all ordinary solvents from a solution of 5 grams of quinine bisulphate in 250 c.c. of water to which 2 grams of potassium ferrocyanide in 10 c.c. of water had been added (Found: Fe=4·42. Calc.: Fe=4·43 per cent.). On dehydration over sulphuric acid, the hemihydrate was obtained (Loss=31·16; 21½H$_2$O requires 30·72 per cent.). Analysis of the hemihydrate gave: C=62·86, 63·03; H=5·83, 6·20. Calc.: C=63·20; H=6·07 per cent.

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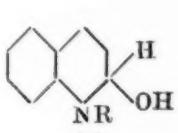
CXV—*The Cyanine Dyes. Part II. The Synthesis of o-Aminocinnamylidenequinaldine Methiodide.*

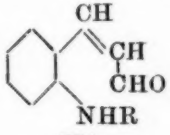
By William Hobson Mills and Percy Edwin Evans.

It has been generally recognised that in the formation of *iso*cyanines by the action of alkalis on mixtures of a quinoline with a quinaldine alkyl iodide, a dominant part is played by the highly reactive ψ-bases to which the action of alkalis on a quinoline alkyl iodide is known to give rise.

Two views are held with respect to the constitution of these ψ-bases. In addition to the cyclic carbinol formula (I) suggested by Decker (*Ber.*, 1892, **25**, 3326), an open-chain alkylamino-



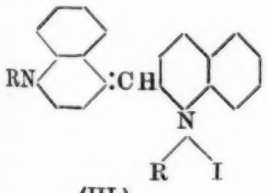
(I.)



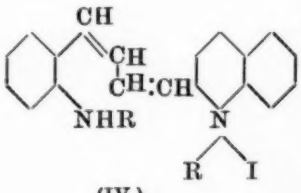
(II.)

aldehyde formula (II) was proposed by Roser (*Annalen*, 1892, **272**, 221; 1894, **282**, 363), and was supported with additional experimental evidence by Gadamer (*Arch. Pharm.*, 1905, **243**, 12; 1908, **246**, 89) and Kaufmann and Strübin (*Ber.*, 1911, **44**, 680).

It was pointed out by W. König (*J. pr. Chem.*, 1912, [ii], **86**, 166) that the possibility that the quinolinium ψ-bases were to be represented by the second of these formulæ made it necessary to take into account a corresponding constitution for the *iso*cyanines. Accordingly, in place of the formula (III) which he had originally proposed (*J. pr. Chem.*, 1906, [ii], **73**, 100) for this class of dyes, he now suggested the open-chain formula (IV), and gave reasons for preferring it to the formulæ which had previously been put forward.



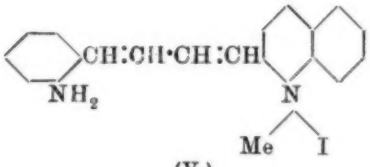
(III.)



(IV.)

With a view to obtain evidence which would bear on the constitution of the *iso*cyanines, we undertook the synthesis of a com-

pound of a type almost identical with that represented by formula IV. This substance was *o-aminocinnamylidenequinaldine methiodide* (V), the structural formula of which only differs from König's butadiene formula for dimethyl*iso*cyanine iodide in that it contains an amino-group in place of a methylamino-group attached to the benzene nucleus in the ortho-position with respect to the butadiene chain.



(V.)

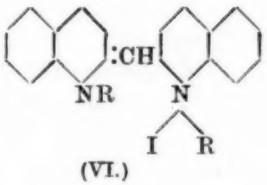
Meanwhile, the facts described in a preceding paper (Mills and Wishart, this vol., 579) were discovered. These showed definitely that the *iso*cyanines do not possess an open-chain formula, and the chief object of these experiments was thus attained in another way; we think, however, that the synthesis and properties of *o*-aminocinnamylidenequinaldine methiodide, which in certain respects bears a distinct relationship to the dyes of the cyanine class, may still be of sufficient interest to be recorded.

The synthesis was effected in the following manner. *o*-Nitrocinnamaldehyde was heated with quinaldine and zinc chloride, when condensation took place, with the formation of *o-nitrocinnamylidenequinaldine*, $NO_2 \cdot C_6H_4 \cdot CH:CH \cdot CH:CH \cdot C_9H_6N$. This was reduced with iron and acetic acid to the corresponding *amino*-compound, which forms deep reddish-brown mono-acid salts and di-acid salts, which are pale yellow and characterised by their sparing solubility.

To prepare the quaternary methiodide of this base, the amino-group was first protected by acylation. The acylamino-compound was then converted into its methiodide by heating with methyl iodide, and finally the acyl group was eliminated. Various acyl derivatives having been examined, the *formyl* compound was found to give the best results, and its *methiodide*, on hydrolysis with dilute hydrochloric acid, gave *o*-aminocinnamylidenequinaldine methiodide (V).

It proved to be a compound which forms deep reddish-brown solutions and crystallises in small, oblique-ended needles showing a dark olive-green metallic reflex; the crystals are strongly pleochroic, but almost opaque. Its strongly coloured aqueous solutions are at once turned pale yellow by the addition of mineral acids, evidently on account of the formation of di-acid salts. It

dyes wool, and especially silk, a beautiful rich reddish-brown, but the colour is surprisingly fugitive in daylight. Its absorption spectrum in the visible region, unlike the spectra of the *iso*cyanines, which are characterised by a distinctive pair of bands, shows only general absorption in the violet and blue, which in more concentrated solutions extends as far as the orange. It has also no appreciable sensitising action on a gelatino-bromide photographic plate. Apart, therefore, from its instability towards light and its partial decolorisation by acids, it shows little analogy in properties to the *iso*cyanines. At the same time, the fact should not be overlooked that, on account of the presence of the two ethylenic linkings in the butadiene chain, a compound of this structure should be capable of existence in four geometrically isomeric forms, only one of which is closely related in configuration to cyanine dyes, namely, those of the at present unknown **α-α**-class (VI), the properties of which can, however, to some extent be inferred from those of the analogous compounds of the benzothiazole series prepared by Hofmann (*Ber.*, 1888, **21**, 2262).



(VI.)

Experimental.

o-Nitrocinnamaldehyde.—We first prepared this substance by the method described by Diehl and Einhorn (*Ber.*, 1885, **18**, 2336), but as the process proved troublesome to carry out, we sought for some method of nitrating cinnamaldehyde by which the *o*-nitro-derivative could be more easily obtained. Experiments on nitration in the presence of acetic anhydride showed that the process could be conducted so that *o*-nitrocinnamaldehyde was the sole crystalline product.

A solution of 25 grams of nitric acid (D 1·50) in 50 grams of glacial acetic acid was dropped slowly, with frequent shaking, into an ice-cold solution of 50 grams of cinnamaldehyde in 200 c.c. of acetic anhydride. The solution was allowed to remain for two days at the ordinary temperature; dilute hydrochloric acid was then added and the mixture well shaken. Considerable heat was developed, and, on cooling, *o*-nitrocinnamaldehyde crystallised in almost colourless needles. By recrystallising once from alcohol, the compound was obtained pure in very pale yellow needles melting

at 127°. This method thus gives a very simple means of preparing *o*-nitrocinnamaldehyde, and although the yield is only 36 per cent. of the weight of cinnamaldehyde taken, it could probably be improved by further investigation of the process.

o-Nitrocinnamylidenequinaldine.—A mixture of *o*-nitrocinnamaldehyde (10 grams), quinaldine (8·1 grams), and zinc chloride (2 grams) was heated on the water-bath for five hours. The resulting crystalline mass was dissolved in hot acetone, and the solution, on cooling, deposited the pure condensation product in yellow rhombs melting at 149°. The compound dissolves readily in hot acetone or chloroform, sparingly in alcohol, benzene, or ether (Found: N = 9·28. $C_{19}H_{14}O_2N_2$ requires N = 9·27 per cent.).

p-*Nitrocinnamylidenequinaldine.*—*p*-Nitrocinnamaldehyde (10 grams) and quinaldine (8·1 grams) were heated together on the boiling-water bath for ten hours. The product was dissolved in alcohol, the solution poured into water, and the yellow solid was collected and crystallised from acetone. Pure p-*nitrocinnamylidenequinaldine* was thus obtained in yellow needles melting at 185·5° (Found: N = 9·25. $C_{19}H_{14}O_2N_2$ requires N = 9·27 per cent.).

o-Aminocinnamylidenequinaldine,

$$NH_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C_9H_6N.$$

—An examination of the action of various reducing agents on *o*-nitrocinnamylidenequinaldine showed that the reduction could be carried out most conveniently by means of iron and acetic acid. The nitro-compound (10 grams) was dissolved in warm glacial acetic acid, the solution diluted with water, and excess of iron added. The mixture, which rapidly became a deep reddish-brown, was kept at 60° for two hours, and the excess of iron was then removed. On adding concentrated hydrochloric acid, the sparingly soluble yellow *dihydrochloride* of the new base was precipitated. It was collected, washed with concentrated hydrochloric acid, and decomposed with ammonia. On crystallising the base thus formed from aqueous alcohol, it was obtained in yellow needles melting at 135·5°. It is very readily soluble in alcohol or chloroform, moderately so in acetone, ether, or benzene, and practically insoluble in water (Found: C = 83·3; H = 5·9; N = 10·2. $C_{19}H_{16}N_2$ requires C = 83·8; H = 5·9; N = 10·3 per cent.).

o-Formylaminocinnamylidenequinaldine,

$$CHO{\cdot}NH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C_9H_6N.$$

—*o*-Aminocinnamylidenequinaldine was heated with excess of 90 per cent. formic acid under reflux on the sand-bath for three hours. After cooling, the mixture was diluted with water, rendered alkaline with ammonia, and the precipitated formyl derivative was

collected and crystallised from alcohol. It formed pale yellow needles melting at 185·5°. This compound is readily soluble in hot alcohol or chloroform, fairly so in acetone, and sparingly so in ether or benzene (Found: N = 9·4. $C_{20}H_{16}ON_2$ requires N = 9·3 per cent.).

o-Formylaminocinnamylidenequinaldine Methiodide.—Formylaminocinnamylidenequinaldine (2 grams) was heated with methyl iodide (6 grams) in a sealed tube at 100° for three hours. The red mass obtained in this way crystallised from alcohol in dark red needles, which melted at 218°. The substance is soluble in hot water or alcohol, sparingly so in acetone or chloroform, and insoluble in ether or benzene (Found: I = 28·7. $C_{21}H_{19}ON_2I$ requires I = 28·7 per cent.).

o-Acetylaminocinnamylidenequinaldine,

$$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot CH{:}CH\cdot CH{:}CH\cdot C_9H_6N.$$

—The amino-compound (10 grams) was heated for one hour on the water-bath with acetic anhydride (30 grams). The excess of acetic anhydride was then decomposed by heating with water, and the acetyl derivative precipitated by the addition of ammonia. It was collected and crystallised from aqueous alcohol, from which it separates in pale yellow needles melting at 179°. It is soluble in chloroform and dissolves very readily in alcohol. It is almost insoluble in ether, acetone, water, or benzene (Found: N = 9·1. $C_{21}H_{18}ON_2$ requires N = 8·9 per cent.).

Acetylaminocinnamylidenequinaldine Methiodide.—The acetyl derivative (2 grams) was heated with methyl iodide (4 grams) in a sealed tube at 100° for three hours. The bright red contents of the tube were crystallised from water, and then recrystallised from alcohol. The methiodide obtained in this way consisted of bright red needles melting at 216—217° (Found: I = 27·75. $C_{22}H_{21}ON_2I$ requires I = 27·85 per cent.).

It is soluble in water, alcohol, or acetone, sparingly so in chloroform, and insoluble in ether or benzene.

Carboxymethylaminocinnamylidenequinaldine,

$$CH_3\cdot CO_2\cdot NH\cdot C_6H_4\cdot CH{:}CH\cdot CH{:}CH\cdot C_9H_6N.$$

—A solution of *o*-aminocinnamylidenequinaldine (2·5 grams) in dry chloroform was heated with methyl chloroformate (1 gram) under reflux for four hours. Water was added, and then ammonia until the red colour of the hydrochloride disappeared. The chloroform layer was separated, the chloroform evaporated, and the residue crystallised from alcohol. The compound formed lustrous, yellow plates melting at 175·5° (Found: N = 8·5. $C_{21}H_{18}O_2N_2$ requires N = 8·5 per cent.).

This compound is readily soluble in hot alcohol or chloroform,

sparingly so in acetone, ether, or benzene, and practically insoluble in water.

o-*Aminocinnamylidenequinaldine Methiodide* (V).—This substance was obtained by the hydrolysis of its acyl derivatives, the reaction being most easily carried out with the formyl compound. Formylaminocinnamylidenequinaldine methiodide is readily hydrolysed by dissolving in hot water, adding a little concentrated hydrochloric acid, and boiling for twenty minutes. To ensure getting the iodide uncontaminated with chloride, potassium iodide was added to the mixture, and the greater part of the acid was then neutralised with ammonia, when a dark reddish-brown precipitate of the iodide was obtained. This was recrystallised from methyl alcohol to which a little aqueous potassium iodide had been added. The salt forms needles with a very dark olive-green lustre melting at 194·5°. It is very readily soluble in methyl alcohol, less so in ethyl alcohol or water, and sparingly so in acetone or chloroform. For analysis it was dried in a vacuum at 70° (Found: C=57·5; H=4·6; N=6·53; I=30·4, 30·8. $C_{20}H_{19}N_2I$ requires C=58·0; H=4·6; N=6·76; I=30·7 per cent.).

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CXVI.—*The Isomerism of the Oximes. Part IX. 2 : 4-Dinitrobenzaldoxime and Bromo-substituted Hydroxy- and Methoxy-benzaldoximes.*

By VERA WENTWORTH and OSCAR LISLE BRADY.

On the Hantzsch-Werner hypothesis, all substituted benzaldoximes should exist in two stereoisomeric forms. In a number of cases, however, all attempts to obtain the unstable isomeride have been unsuccessful (compare Brady and Dunn, T., 1916, **109**, 667), but from a study of these cases there has emerged no underlying principle determining the non-existence of the second form other than the inhibiting effect of the hydroxyl group.

A number of other substituted benzaldoximes have now been investigated with a view to arrive at some generalisation.

The nitrobenzaldoximes all exist in two isomeric forms, and although 2:4-dinitrobenzaldoxime has been prepared (Sachs and Kempf, *Ber.*, 1902, **35**, 1234), its configuration has not been determined. It has been found to possess the *anti*-configuration by the preparation of its acetyl derivative and hydrolysis of this compound to the original oxime according to Hantzsch's method.

It does not, however, form a hydrochloride in the usual way, and all attempts to obtain a second isomeride have been unsuccessful.

In no case has a substituted benzaldoxime containing a hydroxyl group in the nucleus been obtained in two forms, although *p*-acetoxybenzaldoxime and anisaldoxime both give a *syn*-compound. It was thought that substituted hydroxybenzaldoximes, particularly those containing a heavy group in the ortho-position with respect to the hydroxyl group, might exist in two forms, as the entrance of other groups might exert a "steric hindrance" effect. 5-Bromovanillinoxime and 5-nitrovanillinoxime have already been investigated, with negative results (Brady and Dunn, T., 1915, **107**, 1858), and 3:5-dibromo-*p*-hydroxybenzaldoxime and 3:5-dibromo-*o*-hydroxybenzaldoxime have now been studied. The former yields a hydrochloride in the usual way, but this regenerates the original oxime on decomposition with sodium carbonate solution; the latter does not form a hydrochloride, and cannot therefore be converted into an isomeride.

Although anisaldoxime readily gives a *syn*-derivative, *o*-methoxybenzaldoxime and 3:4-dimethoxybenzaldoxime (veratraldoxime) exist only in the *anti*-form. The influence of the introduction of the bromine atom into these compounds has been investigated, and, whilst it has been found that 5-bromo-*o*-methoxybenzaldoxime cannot be converted into a *syn*-isomeride through the hydrochloride, 5-bromo-3:4-dimethoxybenzaldoxime, on the other hand, yields an unusually stable *syn*-derivative, remarkable in that its acetyl derivative is not decomposed to the nitrile by sodium carbonate solution, but only by sodium hydroxide solution.

These results have not made less puzzling the failure to obtain *syn*-isomerides from some substituted benzaldoximes.

It is evident that the introduction of negative substituents is not a determining factor, and the inhibitive effect of the hydroxyl group on the formation of *syn*-isomerides has been further demonstrated. Two more benzaldoximes, which do not give hydrochlorides when treated in dry ethereal solution with dry hydrogen chloride, have been added to the previously unique case of 6-nitropiperonaloxime.

Experimental.

Attempted Conversion of 2:4-Dinitrobenzaldoxime.—The oxime, prepared from the aldehyde, hydroxylamine hydrochloride, and sodium carbonate in alcohol, was dissolved in dry ether and the solution saturated with dry hydrogen chloride. No hydrochloride was precipitated, and evaporation of the ethereal solution in a current of dry air gave the unchanged oxime. An attempt was

made to bring about the conversion by Dunstan and Thole's method (P., 1911, **27**, 233), but without success. Ciamician and Silber (*Ber.*, 1903, **36**, 4268) found that the nitrobenz*anti*aldoximes, when exposed to sunlight in benzene solution in sealed tubes, were converted into the nitrobenz*syn*aldoximes. Similar experiments are being tried with 2:4-dinitrobenzaldoxime and other oximes; the results will be described in a subsequent communication.

Acetyl Derivative.—The configuration of the oxime was determined by the preparation of its acetyl derivative, and the subsequent hydrolysis of this compound to the oxime. The oxime was treated with about four times its weight of acetic anhydride and warmed to 30°. The oxime dissolved, and, on decomposing the excess of acetic anhydride with sodium carbonate solution, the *acetyl* derivative separated; from dilute alcohol it forms yellow, microscopic crystals melting at 79° (Found: Ac=17·4. $C_9H_7O_6N_3$ requires Ac=17·0 per cent.).

On warming with 10 per cent. sodium hydroxide solution for some minutes, the acetyl compound dissolved, and, on addition of dilute sulphuric acid, the original oxime was precipitated. The *anti*-configuration of 2:4-dinitrobenzaldoxime is thus established.

3:5-*Dibromo*-p-*hydroxybenzaldoxime.*—To 28 grams of 3:5-dibromo-*p*-hydroxybenzaldehyde, prepared by Paal's method (*Ber.*, 1895, **28**, 2408), were added 100 c.c. of 10 per cent. sodium hydroxide solution; the aldehyde dissolved, and the sodium salt crystallised out almost immediately. A further 200 c.c. of water was added, together with 8 grams of hydroxylamine hydrochloride in water, and the mixture was left overnight. At the end of that time the precipitated sodium salt of the aldehyde had completely disappeared, and, on acidifying the solution with dilute sulphuric acid, the oxime was precipitated. It crystallises from alcohol in colourless needles melting at 199° (Paal and Kromschröder, *Ber.*, 1895, **28**, 3236, give 194°) (Found: Br=53·9. Calc.: Br=54·2 per cent.).

The *hydrochloride*, prepared by saturating a solution of the oxime in dry ether with dry hydrogen chloride, was precipitated as a white, crystalline powder melting and decomposing at 190° (Found: Cl=10·3. $C_7H_5O_2NBr_2,HCl$ requires Cl=10·7 per cent.). The hydrochloride was decomposed with sodium carbonate solution and the oxime precipitated with dilute sulphuric acid; this was found to be the unaltered *anti*-derivative.

The Diacetyl Derivative.—The oxime is not acetylated with the ease that is usually observed, and one drop of concentrated sulphuric acid is needed as a catalyst. The oxime was covered with acetic anhydride and the sulphuric acid added; the compound

dissolved rapidly, and the liquid became just appreciably warm. Excess of acetic anhydride was removed with sodium carbonate, and the acetyl derivative separated as a gum-like material. This substance was difficult to crystallise, but when dissolved in the minimum amount of boiling absolute alcohol, and the liquid cooled and the walls of the vessel scratched for some minutes, it separated as a white, crystalline powder melting at 122° (Found: Ac=22·8. $C_{11}H_9O_4NBr_2$ requires Ac=22·7 per cent.). When heated for fifteen minutes with 10 per cent. sodium hydroxide, the diacetyl compound regenerates the original oxime, thus establishing the *anti*-configuration of that substance.

3:5-*Dibromo*-o-*hydroxybenzaldoxime*.—The preparation of 3:5-dibromo-*o*-hydroxybenzaldehyde has been described by Heerlein (*Berz. Jahresb.*, **25**, 486) and Werner (*Bull. Soc. chim.*, 1886, [ii], **46**, 277), but a more satisfactory method consists in dissolving salicylaldehyde in glacial acetic acid and adding the calculated quantity of bromine in acetic acid, the mixture being kept cool. After remaining for some time, the addition of water precipitates the aldehyde, which may be crystallised from alcohol. To a solution of 16 grams of the aldehyde in alcohol, 5 grams of hydroxylamine hydrochloride dissolved in a minimum quantity of water were added, followed by 5 grams of sodium hydroxide in concentrated aqueous solution. The mixture was allowed to remain overnight, the oxime precipitated by the addition of excess of dilute sulphuric acid, and crystallised first from alcohol and then from benzene. 3:5-*Dibromo*-o-*hydroxybenzaldoxime* separates from benzene in colourless needles melting at 204° (Found: Br=54·2. $C_7H_5O_2NBr_2$ requires Br=54·2 per cent.).

The *diacetyl* derivative, prepared in the usual way, crystallises from alcohol in colourless needles melting at 111·5° (Found: Ac=22·4. $C_{11}H_9O_4NBr_2$ requires Ac=22·7 per cent.). On hydrolysis with 10 per cent. sodium hydroxide, the diacetyl compound regenerated the original oxime, which is accordingly the *anti*-isomeride.

5-*Bromo*-o-*methoxybenzaldoxime*.—5-Bromo-*o*-methoxybenzaldehyde was prepared by Perkin (*Annalen*, 1868, **145**, 304) by the bromination of *o*-methoxybenzaldehyde; it may, however, be more economically prepared from 5-bromosalicylaldehyde, obtained by the bromination of salicylaldehyde (Piria, *Annalen*, 1839, **30**, 171). Twenty grams of 5-bromosalicylaldehyde were dissolved in a solution of 8 grams of sodium hydroxide in 200 c.c. of water, and 24 grams of methyl sulphate added with constant shaking. The methyl ether separated as a solid, and, after some time, was collected and crystallised from alcohol. Ten grams of the aldehyde

were dissolved in 50 c.c. of alcohol, and 4 grams of hydroxylamine hydrochloride and 4 grams of sodium hydroxide, each dissolved in the minimum quantity of water, were added. After remaining overnight, the oxime was precipitated by acidifying with dilute sulphuric acid, and crystallised from methyl alcohol, from which it separated in long, colourless needles melting at 109° (Found: Br = 34·5. $C_8H_8O_2NBr$ requires Br = 34·8 per cent.).

The *acetyl* derivative crystallises from alcohol in colourless prisms melting at 102° (Found: Ac = 15·3. $C_{10}H_{10}O_3NBr$ requires Ac = 15·8 per cent.). Hydrolysis of this compound to the original oxime with sodium hydroxide solution established the *anti*-configuration of the latter.

Hydrochloride of 5-*Bromo*-o-*methoxybenzaldoxime*.—The oxime was dissolved in dry ether and the solution saturated with dry hydrogen chloride. The hydrochloride was precipitated as a yellow, crystalline powder melting and decomposing at 123° (Found: Cl = 13·1. $C_8H_8O_2NBr,HCl$ requires Cl = 13·3 per cent.). The hydrochloride, on decomposition with sodium carbonate solution, gave a crude oxime melting at 100°. Part was recrystallised from acetone and water, when it gave a compound, which was proved to be the original oxime by the method of mixed melting points. The rest was treated with acetic anhydride, and gave the acetyl derivative, which, on hydrolysis, gave the original oxime. Accordingly, no conversion to the *syn*-isomeride had taken place.

5-*Bromo*-3:4-*dimethoxybenz*anti*aldoxime*.—Eighteen grams of 5-bromoveratraldehyde, prepared from 5-bromovanillin by methylation with methyl sulphate (Dakin, *Amer. Chem. J.*, 1909, **42**, 494), were dissolved in 50 c.c. of alcohol, and 6 grams of hydroxylamine hydrochloride and 3 grams of sodium hydroxide, each in the minimum amount of water, were added. After remaining overnight, the oxime was precipitated by the addition of dilute sulphuric acid and recrystallised from dilute alcohol, when it separated in colourless, shining needles melting at 83° (Found: Br = 30·4. $C_9H_{10}O_3NBr$ requires Br = 30·8 per cent.).

The *acetyl* derivative was prepared in the usual way, and its hydrolysis confirmed the *anti*-configuration of the original oxime. It crystallises with difficulty from dilute methyl alcohol in microscopic crystals melting at 77° (Found: Ac = 14·3. $C_{11}H_{12}O_4NBr$ requires Ac = 14·2 per cent.).

Hydrochloride of 5-*Bromo*-3 : 4-*dimethoxybenzaldoxime*.—The *anti*-oxime was dissolved in dry ether and the solution saturated with dry hydrogen chloride, when the hydrochloride was precipitated as a white, crystalline powder melting and decomposing at 120—125° (Found: Cl = 11·8. $C_9H_{10}O_3NBr,HCl$ requires Cl = 12·0 per cent.).

*5-Bromo-3 : 4-dimethoxybenz*syn*aldoxime.*—The above hydrochloride was decomposed with sodium carbonate solution, and the crude oxime melted at 108°. Crystallisation from acetone and water gave the pure syn-*oxime* in small prisms melting at 116° (Found: Br = 30·9. $C_9H_{10}O_3NBr$ requires Br = 30·8 per cent.).

Acetyl Derivative.—The *syn*-oxime was treated with about four times its weight of acetic anhydride, the solution warmed to 30°, and the excess of acetic anhydride decomposed with sodium carbonate solution. Unlike the acetyl derivatives of other *syn*-oximes that have been studied, that derived from 5-bromo-3:4-dimethoxybenz*syn*aldoxime is not decomposed in these circumstances with the formation of nitrile, and the solid which separated proved to be the acetyl derivative. When crystallised from dilute alcohol, it tended to separate as an oil, which slowly solidified, but after two recrystallisations it melted sharply at 73° (Found: Ac = 13·9. $C_{11}H_{12}O_4NBr$ requires Ac = 14·2 per cent.).

The *acetyl* derivative was warmed with 10 per cent. sodium hydroxide solution to 35°. After cooling and diluting, the solid was crystallised from alcohol, and found to be 5-bromoveratronitrile (m. p. 117°), giving, on boiling with sodium hydroxide, ammonia and 5-bromoveratric acid.

5-Bromoveratronitrile.—For the purpose of identification of the product obtained by treating the above acetyl compound with sodium hydroxide, the nitrile was prepared by boiling 5-bromo-3:4-dimethoxybenz*anti*aldoxime with excess of acetic anhydride for three hours. The excess of anhydride was decomposed with sodium carbonate solution, and the solid was crystallised from alcohol, when the nitrile separated in colourless, microscopic crystals melting at 117° (Found: Br = 32·8. $C_9H_8O_2NBr$ requires Br = 33·1 per cent.).

The nitrile, on boiling for thirty minutes with 10 per cent. sodium hydroxide solution, is completely hydrolysed, and, on acidifying the solution, 5-bromoveratric acid (m. p. 189°) is precipitated. Zincke and Francke (*Annalen*, 1896, **293**, 183), who obtained this acid from methyl 5-bromoprotocatechuate by methylation and subsequent hydrolysis, give 191° as the melting point, and Pschorr (*Annalen*, 1912, **391**, 31), who obtained it by the oxidation of 5-bromoveratraldehyde, gives 192—193°.

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CXVII.—*The Constitution of Carbamides. Part XI. The Mechanism of the Synthesis of Urea from Ammonium Carbamate. The Preparation of certain Mixed Tri-substituted Carbamates and Dithiocarbamates.*

By Emil Alphonse Werner.

In 1868 Basarov (*J. pr. Chem.*, [ii], **1**, 283; *Journ. Chem. Soc.*, **21**, 194) obtained urea by the action of heat on ammonium carbamate under pressure. The change, which is supposed to be obviously explained by the simple equation

$$CO\langle^{NH_2}_{O\cdot NH_4} = CO\langle^{NH_2}_{NH_2} + H_2O,$$

is always considered to represent the converse of the ultimate hydrolysis of urea to ammonium carbonate, and for this reason this synthesis is commonly cited as evidence *par excellence* in favour of the deceptive "carbamide" configuration.*

To satisfy this view, it has been assumed, without any proof, that water is eliminated from the group $\cdot O\cdot NH_4$, the production of urea being thus analogous to the formation of acetamide from ammonium acetate, or of oxamide from ammonium oxalate. As a matter of fact, the mechanism of the formation of urea in this reaction is of quite a different order, since it is nothing more than a modification of Wöhler's synthesis, namely, the production of urea from ammonia and cyanic acid (HN:CO) as the result of the following series of changes:

$$(1)\ CO\langle^{NH_2}_{O\cdot NH_4} \rightarrow CO\langle^{NH_2}_{OH} + NH_3;\ (2)\ CO\langle^{NH_2}_{OH} \rightarrow (HO\cdot CN \rightleftharpoons HN{:}CO) + H_2O;\ (3)\ NH_3 + HN{:}CO \rightarrow HN{:}C\langle^{NH_2}_{O}.$$

So far as ammonium carbamate is concerned, the fact that urea and ammonium cyanate were found in the product after vaporising the salt through a glass tube heated to incipient redness is not final proof that cyanic acid was produced as shown above, since Mixter (*Amer. Chem. J.*, 1882, **4**, 35) obtained urea from carbon

* It may be of interest to record that Kolbe, in presenting Basarov's paper to the Society, opens with the words: "From the conviction that urea is not carbamide"—a remark which, the author is equally convinced, has been fully justified.

dioxide and ammonia at a red heat. There can be no doubt that cyanic acid was generated in this case, thus,

$$CO_2 + NH_3 * = HN{:}CO + H_2O$$

(see Expt. VI), as Mixter suggested.

Convincing evidence, however, in support of the above series of changes has been obtained from a study of the decomposition of certain substituted ammonium carbamates and dithiocarbamates.

Fichter and Becker (*Ber.*, 1911, **44**, 3473, 3481) showed that methylammonium methylcarbamate, $NHMe{\cdot}CO{\cdot}O{\cdot}NH_3Me$, and the ethylammonium analogue gave the respective symmetrical disubstituted carbamides, whilst no tetra-substituted carbamide could be obtained from diethylammonium diethylcarbamate. Since direct dehydration of the carbamates was assumed to represent the mechanism of the change, it follows that if the reaction

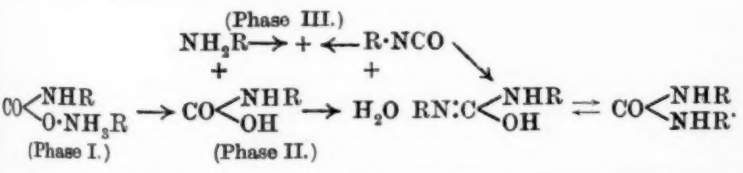
$$(a)\quad CO\langle{}^{NHR}_{O{\cdot}NH_3R} \longrightarrow CO\langle{}^{NHR}_{NHR} + H_2O$$

was the result of the direct elimination of water from the group $\cdot O{\cdot}NH_3R$, there seemed no reason why the change

$$(b)\quad CO\langle{}^{NR_2}_{O{\cdot}NH_2R_2} \longrightarrow CO\langle{}^{NR_2}_{NR_2} + H_2O$$

should not take place with even greater facility than in the case of reaction (*a*). Since loss of water could take place in one way only, and considering the stability of tetra-substituted carbamides, these investigators were unable to explain the apparent abnormality.

Now, according to the three-phase change, or "dissociation theory" here put forward, only carbamates which contain the system $\cdot CO{\cdot}NHR$, capable of yielding $R{\cdot}NCO$, can give rise to substituted carbamides. Thus, in the decomposition of all such carbamates, change (*a*), for example, is correctly represented by the following general scheme:



* This reaction may prove to be of considerable importance in the near future as a method for the fixation of nitrogen as urea, since it very probably only awaits the discovery of a suitable catalyst to realise the change on an economic scale. Of great interest, in this connexion, is the recent discovery by Mailhe (*Ann. Chim.*, 1920, [ix], **13**, 226) that the change $CO + NH_3 = HCN + H_2O$ is quantitative at 430—450° in the presence of thorium oxide.

Whilst under normal pressure carbamic acid and its mono-substituted homologues are decomposed, thus,

$$CO<^{NHR}_{OH} \longrightarrow CO_2 + NH_2R,$$

this change must be largely suppressed under high pressure in favour of the alternative one represented by phase II. In the case of a disubstituted carbamic acid, the change

$$CO<^{NR_2}_{OH} \longrightarrow CO_2 + NHR_2$$

alone prevails, and hence a tetra-substituted carbamide is not formed.

The soundness of the present theory has been experimentally tested by proving, as predicted by the scheme, that carbamates of type (*c*), $CO<^{NHR}_{O\cdot NH_2R_2}$, yielded tri-substituted carbamides (as the result of phase III, $RNCO + NHR_2 = CO<^{NR_2}_{NHR}$), whilst those of type (*d*), $CO<^{NR_2}_{O\cdot NH_3R}$, did not. Carbamates of the latter types, which have not been hitherto described, were successfully prepared by a method based on the differences in the relative strengths of the amines, to which the author has recently drawn attention (T., 1918, **113**, 899; 1919, **115**, 1012).

Benzylammonium benzylcarbamate in cold alcoholic solution was quantitatively decomposed by dimethylamine, thus:

$$CO<^{NH\cdot CH_2Ph}_{O\cdot NH_3\cdot CH_2Ph} + NHMe_2 = CO<^{NH\cdot CH_2Ph}_{O\cdot NH_2Me_2} + CH_2Ph\cdot NH_2$$

Type (*c*).

Dimethylammonium benzylcarbamate gave, after four hours at 140—150° in a sealed tube, *benzyldimethylcarbamide*,

$$NMe_2\cdot CO\cdot NH\cdot CH_2Ph.$$

Diethylammonium benzylcarbamate gave, under like conditions, *benzyldiethylcarbamide*.

Methylammonium diethylcarbamate, $NH_3Me\cdot O\cdot CO\cdot NEt_2$ (type *d*), was prepared by the displacement of diethylamine from diethylammonium diethylcarbamate by the stronger amine, methylamine. After four hours at 145—150°, it failed to yield any methyldiethylcarbamide (Expt. V).

It is obvious that the theory of the direct dehydration of carbamates, which fails entirely to explain the facts just recorded, must be abandoned in favour of the dissociation theory. As a logical sequence thereof, Basarov's synthesis of urea can no longer be upheld as evidence of the "carbamide" structure.

The Decomposition of Dithiocarbamates.

It is well known that dithiocarbamates derived from the interaction of carbon disulphide and primary amines, namely, $RHN{\cdot}CS{\cdot}S{\cdot}NH_2R$ (type *e*), yield symmetrical disubstituted thiocarbamides, whilst those derived from secondary amines, namely, $R_2N{\cdot}CS{\cdot}S{\cdot}NH_2R_2$ (type *f*), do not yield tetra-substituted thiocarbamides.

A study of the decomposition of the following "mixed" dithiocarbamates, of types which have not been hitherto prepared, has proved that the mechanism of the changes is similar to that of carbamates.

Dimethylammonium benzyldithiocarbamate,

$$NH_2Me_2{\cdot}S{\cdot}CS{\cdot}NH{\cdot}CH_2Ph,$$

prepared from benzylammonium benzyldithiocarbamate by the displacement of benzylamine by dimethylamine (Expt. III), gave *benzyldimethylthiocarbamide*, $NMe_2{\cdot}CS{\cdot}NH{\cdot}CH_2Ph$, after an alcoholic solution was boiled under reflux until hydrogen sulphide ceased to be evolved.

Diethylammonium benzyldithiocarbamate,

$$NH_2Et_2{\cdot}S{\cdot}CS{\cdot}NH{\cdot}CH_2Ph,$$

similarly gave *benzyldiethylthiocarbamide* (Expts. III and IV).

Since dithiocarbamates of type (*f*) which contain the system $\cdot S{\cdot}NH_2R_2$ do not yield thiocarbamides, there can be no doubt that the above results were the outcome of a reaction between NHR_2 and $C_6H_5{\cdot}CH_2{\cdot}NCS$ (phase III), produced in accordance with the general scheme.

To prove that thiocarbamates of type (*g*), $NH_3R{\cdot}S{\cdot}CS{\cdot}NR_2$, did not yield tri-substituted thiocarbamides, *methylammonium dimethyldithiocarbamate* (m. p. 90—91°) and *methylammonium diethyldithiocarbamate*, large, hexagonal prisms (m. p. 103°), were prepared. In each case, methylamine and hydrogen sulphide were evolved when alcoholic solutions of the respective salts were heated to 100° under reflux. Whilst no tri-substituted thiocarbamide could be isolated from the product, the main change was a bimolecular decomposition of the acid, $R_2N{\cdot}CS{\cdot}SH$, produced by dissociation of the original salt, as the preliminary change. The theory that the formation of substituted thiocarbamides from dithiocarbamates is simply a direct elimination of hydrogen sulphide is therefore a fallacy.

The well-known fact that ammonium dithiocarbamate, $H_2N{\cdot}CS{\cdot}SNH_4$, yields only ammonium thiocyanate when decomposed by heat under normal pressure is due to the change occurring

below the temperature at which an equilibrium, $HS{\cdot}CN \rightleftharpoons HN{:}CS$, can obtain, the form $HN{:}CS$ being essential to the production of thiourea by its union with ammonia (T., 1912, **101**, 2184; 1919, **115**, 1169).

The Preparation of "Mixed" Dithiocarbamates.

Apart from their theoretical interest, the preparation of dithiocarbamates of types $CS<^{NHR'}_{S\cdot NH_2R_2''}$ and $CS<^{NHR'}_{S\cdot NH_3R''}$ is of some practical importance, since it provides a simple means for obtaining various mixed di- and tri-substituted thiocarbamides by dispensing with the preparation of the otherwise necessary thiocarbimide, R·NCS.

The "displacement" method is not recommended when there is only a small difference between the relative strengths of the amines; thus, in order to realise the reaction,

$$CS<^{NHEt}_{S\cdot NH_3Et} + NH_2Me = CS<^{NHEt}_{S\cdot NH_3Me} + NH_2Et,$$

it was necessary to use a considerable excess of methylamine (3—4 molecules) to complete the change within a reasonable time. On the other hand, *n*-butylamine, for example, was readily displaced from n-*butylammonium* n-*butyldithiocarbamate*, $C_9H_{22}N_2S_2$, by dimethylamine, with the production of *dimethylammonium* n-*butyldithiocarbamate*, $C_7H_{18}N_2S_2$ (refractive hexagonal prisms, m. p. 93·5°).

With closely related amines, admirable results were obtained by dissolving the amine hydrochloride in either an aqueous or alcoholic solution of the sodium salt of the particular dithiocarbamic acid, prepared according to the method described by Delépine (*Compt. rend.*, 1907, **144**, 1126).

Diethylammonium methyldithiocarbamate (prisms, m. p. 89—90°), which could only be prepared according to the equation

$$CS<^{NHMe}_{S\cdot Na} + NHEt_2,HCl = CS<^{NHMe}_{S\cdot NH_2Et_2} + NaCl,$$

gave methyldiethylthiocarbamide in a yield equal to 72 per cent. of the theoretical.

Dimethylammonium ethyldithiocarbamate,

$$NH_2Me_2\cdot S\cdot CS\cdot NHEt,$$

(m. p. 101°), from sodium ethyldithiocarbamate and dimethylammonium chloride, gave a yield of dimethylethylthiocarbamide equal to 67 per cent. of the theoretical.

Experimental.

Preparation of Mixed Benzylcarbamates and Benzyl Dithiocarbamates.

Expt. I.—Thirteen grams of benzylammonium benzylcarbamate (m. p. 101°), prepared by passing carbon dioxide through a solution of benzylamine in dry ether, were placed in a stout tube of soft glass, and 3·5 grams of dimethylamine dissolved in 20 c.c. of alcohol were added. A clear solution was obtained after the mixture had remained at the ordinary temperature for twenty-four hours, when 40 c.c. of ether were added. The viscous *dimethylammonium benzylcarbamate* was allowed to subside, after which the mixture of ether and alcohol, which contained free benzylamine, was poured off. The product was twice treated with 15 c.c. of ether to remove all free amines (Found, by hydrolysis with ammoniacal calcium chloride and titrating the calcium carbonate with hydrochloric acid: CO_2=21·73. $C_{10}H_{16}O_2N_2$ requires CO_2=22·44 per cent.). The tube was sealed, and, after heating at 140° for four hours, the semi-solid product was extracted with water. The insoluble *benzyldimethylcarbamide* (2·6 grams) crystallised from alcohol in colourless, glistening needles, which melted at 166° (Found: N=15·81. $C_{10}H_{14}ON_2$ requires N=15·73 per cent.). The yield was equal to 29·2 per cent. of the theoretical. A specimen prepared from benzyl cyanate and dimethylamine had the same melting point and a similar appearance.

Expt. II.—This was a repetition of I with diethylamine in place of the methyl compound. From *diethylammonium benzylcarbamate*, a viscous liquid, 3·7 grams of *benzyldiethylcarbamide*, slender, glistening prisms melting at 169—170°, in a yield equal to 36 per cent. of the theoretical, were isolated (Found: N=13·66. $C_{12}H_{18}ON_2$ requires N=13·59 per cent.).

Expt. III.—Carbon disulphide (3·8 grams) was added to benzylamine (10·7 grams) in 25 c.c. of alcohol. To the benzylammonium benzyldithiocarbamate formed, dimethylamine (4·7 grams) in 20 c.c. of alcohol was added. After twenty-four hours, 9 grams of *dimethylammonium benzyldithiocarbamate*, brilliant, small, rhomboidal prisms, were collected (m. p. 116—117°) (Found: S=28·19. $C_{10}H_{16}N_2S_2$ requires S=28·07 per cent.).

Five grams of the salt, in 30 c.c. of alcohol, were boiled under reflux until evolution of hydrogen sulphide had ceased. On adding water, *benzyldimethylthiocarbamide* was precipitated in slender, rhombic prisms melting at 95—96°. The yield (3·2 grams) was equal to 75·3 per cent. of the theoretical (Found: S=16·39; N=14·55. $C_{10}H_{14}N_2S$ requires S=16·49; N=14·43 per cent.).

below the temperature at which an equilibrium, $HS{\cdot}CN \rightleftharpoons HN{:}CS$, can obtain, the form HN:CS being essential to the production of thiourea by its union with ammonia (T., 1912, **101**, 2184; 1919, **115**, 1169).

The Preparation of "Mixed" Dithiocarbamates.

Apart from their theoretical interest, the preparation of dithiocarbamates of types $CS<^{NHR'}_{S{\cdot}NH_2R_2''}$ and $CS<^{NHR'}_{S{\cdot}NH_3R''}$ is of some practical importance, since it provides a simple means for obtaining various mixed di- and tri-substituted thiocarbamides by dispensing with the preparation of the otherwise necessary thiocarbimide, R·NCS.

The "displacement" method is not recommended when there is only a small difference between the relative strengths of the amines; thus, in order to realise the reaction,

$$CS<^{NHEt}_{S{\cdot}NH_3Et} + NH_2Me = CS<^{NHEt}_{S{\cdot}NH_3Me} + NH_2Et,$$

it was necessary to use a considerable excess of methylamine (3—4 molecules) to complete the change within a reasonable time. On the other hand, *n*-butylamine, for example, was readily displaced from n-*butylammonium* n-*butyldithiocarbamate*, $C_9H_{22}N_2S_2$, by dimethylamine, with the production of *dimethylammonium* n-*butyldithiocarbamate*, $C_7H_{18}N_2S_2$ (refractive hexagonal prisms, m. p. 93·5°).

With closely related amines, admirable results were obtained by dissolving the amine hydrochloride in either an aqueous or alcoholic solution of the sodium salt of the particular dithiocarbamic acid, prepared according to the method described by Delépine (*Compt. rend.*, 1907, **144**, 1126).

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(m. p. 101°), from sodium ethyldithiocarbamate and dimethylammonium chloride, gave a yield of dimethylethylthiocarbamide equal to 67 per cent. of the theoretical.

EXPERIMENTAL.

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Expt. IV.—When diethylamine (5·4 grams) replaced dimethylamine in the previous experiment, 9·7 grams of *diethylammonium benzyldithiocarbamate*, stout, hexagonal prisms melting at 111°, were obtained (Found: S=25·17. $C_{12}H_{20}N_2S_2$ requires S=25·0 per cent.). Five grams gave *benzyldiethylthiocarbamide* (3·42 grams), silky needles melting at 67°, in a yield equal to 79 per cent. of the theoretical (Found: S=14·29. $C_{12}H_{18}N_2S$ requires S=14·41 per cent.).

Methylammonium Diethylcarbamate.

Expt. V.—Diethylammonium diethylcarbamate (10 grams), prepared by the union of carbon dioxide and the vapour of pure diethylamine, as recommended by Fichter and Becker (*loc. cit.*), was allowed to remain for twenty-four hours in contact with a solution of methylamine (6 grams) in a mixture of ether and alcohol contained in a separating funnel. The viscous liquid was subjected to a second treatment with methylamine (3 grams), after which it was well extracted with pure ether to remove all free amine. It gave no precipitate with a solution of calcium chloride in the cold, but a copious precipitate of calcium carbonate when warmed [Found: CO_2 (on hydrolysis)=29·06. $C_6H_{16}O_2N_2$ requires CO_2=29·72 per cent.]. The original ethyl compound requires CO_2=23·15 per cent., hence the displacement of the diethylammonium group was practically complete. Five grams heated for four hours in a sealed tube at 140—150° gave a product which volatilised completely at 100°. No methyldiethylcarbamide, therefore, was formed.

Formation of Urea and Ammonium Cyanate from Ammonium Carbamate.

Expt. VI.—Ammonium carbamate, contained in a flask attached to a tube of hard glass (120 cm. long and 1·5 cm. bore), was vaporised in a current of dry ammonia, while the tube was maintained at a low red heat over a length of 80 cm., the forward portion being cooled by a circulating current of water. The presence of ammonium cyanate in the sublimate, which was collected, was proved by the formation of a precipitate of silver cyanate in a solution of the product carefully neutralised by nitric acid to which silver nitrate had been previously added to avoid loss of cyanic acid by hydrolysis. Urea was detected by the xanth-hydrol reaction and by the formation of its nitrate.

Whilst this experiment may be considered a repetition of

Mixter's (*loc. cit.*), the presence of ammonium cyanate, which was not pointed out by this investigator, is of much theoretical interest, since, in the author's opinion, it is formed side by side with urea, and not necessarily from the latter, generated beforehand.

Summary.

(1) The formation of urea from ammonium carbamate is no evidence of the "carbamide" structure, since it arises from the interaction of ammonia and cyanic acid (HN:CO), as in Wöhler's synthesis.

(2) A scheme which explains the formation of substituted ureas and thioureas from substituted carbamates and thiocarbamates, and is in agreement with all the known facts, has been experimentally proven.

(3) Methods for the preparation of "mixed" dithiocarbamates are described, from which corresponding di- and tri-substituted thioureas may be conveniently obtained.

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[*Received, July 27th*, 1920.]

CXVIII.—*A Comparative Study in the Xanthone Series. Part I.*

By SURENDRA NATH DHAR.

IN the series of investigations of which this is Part I, it is intended to compare xanthone with other compounds having similarities in structure or properties. In the first place, such a comparison is attempted with anthraquinone, which has the greatest similarity to xanthone. No comparative study seems to have been made systematically by anyone except Hertzig (*Monatsh.*, 1891, **12**, 161), who found that euxanthone is more stable than quercetin (a flavone), and Graebe and Eichengrün (*Ber.*, 1891, **24**, 967), who compared some hydroxyxanthones with certain hydroxyanthraquinones and hydroxybenzophenones. Other attempts at a comparison of xanthone with anthraquinone with respect to the colouring properties of their hydroxy-derivatives are evidenced from a few isolated instances. Thus Graebe and Aders (*Annalen*, 1901, **318**, 365) showed the similarity of the hydroxyl group in position 1 in both the series. A. G. Perkin and Everest

have incidentally raised the same question ("The Natural Organic Colouring Matters," pp. 126—127). They compare alizarin with 3:4-dihydroxyxanthone, but, as a matter of fact, 1:2-dihydroxyxanthone, and not the 3:4-derivative, corresponds with alizarin. Attempts are being made to synthesise 1:2-dihydroxyxanthone, and the results will be communicated in due course. At the same time, a systematic comparison is being attempted in the following directions: (1) nitration; (2) direct displacement of nitro-groups by halogens, methoxy-group, etc., and certain other important reactions with nitro-compounds, such as Skraup's synthesis, Doebner and Miller's and Knorr's syntheses, etc.; (3) halogenation; (4) mobility of halogen atoms; (5) migration of diazo-groups.

It is interesting to note that xanthone has been found to be much more reactive than anthraquinone. Thus with nitric acid alone, xanthone gives two dinitroxanthones (α and β), whereas anthraquinone gives a mononitro-derivative only (*Ber.*, 1883, **16**, 363). Again, quite a number of tri- and tetra-nitroxanthones have very easily been prepared, whilst no such polynitro-derivatives of anthraquinone are known, and further nitration of the dinitro-compounds has not yet been effected.

Xanthone seems not only to be more reactive, but also more stable, although from the structure of these compounds such a fact is quite unexpected. It is well known that when fused with potassium hydroxide, xanthone decomposes into 1:1′-dihydroxybenzophenone, whereas anthraquinone is completely degraded to two molecules of benzoic acid. Similarly, it has been found that when further nitration of 1:5- or 1:8-dinitroanthraquinone is attempted with mixtures of nitric and sulphuric acids, they decompose completely, whilst both α- and β-dinitroxanthones are converted into tetranitroxanthones at an earlier stage of such a treatment, and the products are not decomposed on subsequent treatment. It may also be noted that tetrabromoxanthone is nitrated and not decomposed by such a mixture (Dhar, T., 1916, **109**, 740).

So far as the behaviour of nitroxanthone has been studied, it has been found that the nitro-groups in the xanthone series are much more readily displaced by direct bromination than is the case in the anthraquinone series (see this vol., p. 994).

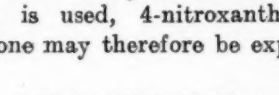
Skraup's synthesis is effected much more readily in the xanthone series than in the anthraquinone series, and xanthone has also been found to be much more reactive towards halogens than anthraquinone. Thus two hexabromo- and an octabromoxanthone have been prepared, whereas no such corresponding

bromo-compounds are known in the anthraquinone series. When treated with bromine in sealed tubes, xanthone gives the 2:7-dibromo-derivative (Graebe, *Annalen*, 1889, **254**, 284), whilst anthraquinone gives 1:2-dibromoanthraquinone.

Theory of the Formation of Xanthone.

Strohbach has discussed in detail the various theories put forward to explain the formation of xanthone (*Ber.*, 1901, **34**, 4136). He attacked mainly the theories of Graebe and Seifert, and, after proving them incapable of explaining all the experimental facts then known, he tried to establish a new theory of his own, together with a few empirical rules. One thing is, however, common to all the theories, and that is the supposition that phenol does not take part in the formation of xanthone or its derivatives. On the other hand, if phenol is supposed to take part in the reaction, the formation of xanthone becomes very simple and does not necessitate the supposition of various intermediate products, the existence of which is doubtful, or any transposition of groups which Strohbach was compelled to make. Thus, in order to ascertain whether phenol takes part or not, experiments were made on the preparation of xanthone from salicylic acid, using in each case an equimolecular proportion of phenol. It is remarkable that the yield of xanthone in each case was just double when phenol was employed. That phenol actively takes part in the reaction and raises the yield in such a remarkable and systematic way is proved beyond doubt by the facts that when nitrobenzene is used instead of phenol, no increase in the yield of xanthone is effected, and when *o*-nitrophenol is used, 4-nitroxanthone is obtained. The formation of xanthone may therefore be explained thus:

$$\underset{\text{Salicylic acid.}}{C_6H_4(OH)\cdot CO_2H} + \underset{\text{Phenol.}}{C_6H_5\cdot OH} = C_6H_4(O\cdot C_6H_5)\cdot CO_2H + H_2O$$



$$C_6H_4 < \begin{matrix} O \\ CO \end{matrix} > C_6H_4 + H_2O$$

Xanthone.

When only salicylic acid is used, half is decomposed into phenol, and traces of phenol can actually be detected in such experiments. The use of a dehydrating agent increases the yield by removing the water formed in the reaction. When acetic anhydride is used, the first reaction is most probably the acetylation of the phenolic group, and this seems to be an important factor in the yield. That is why *o*-acetoxybenzoic acid gives xanthone, and the yield is not affected in the least whether acetic anhydride is used or not.

Now the formation of xanthone from phenyl salicylate, as well as all the other typical instances cited by Strohbach, may be explained by this theory, and the yield is necessarily poor when neither the phenolic groups are acetylated nor any dehydrating agent is used. Thus the formation of xanthone from phenyl salicylate proceeds according to Graebe's first two equations (*loc. cit.*), and the liberated salicylic acid and phenol are not wasted, as he has supposed, but give xanthone again, although the yield in such a case is quite inappreciable, as will be shown in the experimental part (p. 1061). The formation of 5-methyl- and 4:5-dimethyl-xanthone from phenyl homosalicylate supplies another instance in support of this theory. Thus:

$$\underset{\text{Phenyl homosalicylate.}}{C_6H_3Me(OH)\cdot CO_2\cdot C_6H_5} \longrightarrow C_6H_3Me(O\cdot C_6H_5)\cdot CO_2H \longrightarrow$$

$$C_6H_3Me\begin{<}O\\CO\end{>}C_6H_4 + H_2O$$

5-Methylxanthone.

The water formed here hydrolyses one molecule of the ester, giving phenol and homosalicylic acid, which may give a further amount of the same methylxanthone, but the main reaction takes the following course. One of a pair of homosalicylic acid molecules gives *o*-cresol, just as salicylic acid gives phenol, and the condensation takes place in the usual way, giving 4:5-dimethylxanthone. It is interesting to note that, according to Graebe's theory, only 5-methylxanthone, and according to Strohbach's theory, only 4:5-dimethylxanthone, is possible, and according to Seifert's theory none of these is possible, whereas, according to the present theory, both products can be formed. The other instances cited in Strohbach's paper may be explained similarly.

After elucidating the mechanism of the formation of xanthone, a few experiments were made in order to ascertain whether the change takes place gradually or suddenly, and in the case of a sudden change to find the temperature at which it takes place. The temperature of the reaction mixture was therefore recorded, particularly carefully when a single substance was used. The results show conclusively that the conversion takes place gradually, as there was no sudden change in the temperature. Attempts have also been made to synthesise xanthone by various other methods, and it has been found that the condensation of *o*-chlorobenzoic acid with phenol (Ullmann's method) gives most satisfactory results, the yield of xanthone being almost theoretical and the process very simple.

o-Thiolbenzoic acid condenses with benzene and its simple deriv-

atives in the presence of sulphuric acid, giving thioxanthone and its derivatives (*Annalen*, 1896, **149**, 250), but salicylic acid does not condense with benzene or its derivatives either under these conditions or under the influence of phosphoryl chloride or with acetic anhydride in sealed tubes.

Fluorescence of Xanthone and its Derivatives.

The fluorescence of the two nitroxanthones (2- and 3-) is rather unexpected, as it is generally found that the introduction of a nitro-group destroys the fluorescence (Ullmann, *Annalen*, 1907, **355**, 312). Still more striking is the fact that the colour of the fluorescence is deeper in the case of the nitro-compounds. Thus xanthone shows only blue fluorescence, whereas 2- and 3-nitroxanthone show greenish-blue and green fluorescence respectively. Very few di-derivatives of a fluorescent substance are found to be fluorescent, and of all the di-derivatives described in this paper, only dichloroxanthone is fluorescent.

Nitroxanthones.

Only four nitro-derivatives of xanthone have been described. One (3-nitroxanthone) was prepared by Ullmann by condensing 2-chloro-4-nitrobenzoic acid with phenol (*Annalen*, 1904, **355**, 341), and 2:4-dinitroxanthone was prepared by Mayer (*Ber.*, 1909, **42**, 1132) by a similar method. The other two (α- and β-dinitroxanthones) were prepared by Perkin (T., 1883, **43**, 1870) by the direct nitration of xanthone with nitric and sulphuric acids. By a slight modification of this method, these compounds were obtained in a purer condition (T., 1916, **109**, 746), but it has now been found that they can be prepared from xanthone by treating it with nitric acid alone. As has been stated, xanthone differs from anthraquinone in its remarkable capacity for yielding nitro-derivatives, and the number of these has been increased from four to fifteen, and it is expected that many more can be prepared without difficulty. Two methods have mainly been employed, namely, nitration and synthesis by Ullmann's method (*loc. cit.*).

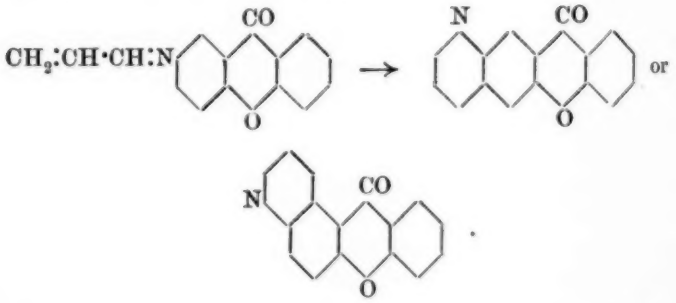
3-Nitroxanthone, which had previously been obtained only by synthesis, has now been prepared by the careful nitration of xanthone. The other three isomeric mononitroxanthones have been obtained by synthesis. 4-*Nitroxanthone* is formed when salicylic acid and *o*-nitrophenol are heated with acetic anhydride, but it has not been possible to obtain this compound by the condensation of *o*-chlorobenzoic acid with *o*-nitrophenol. The remarkable fact has been observed that nitroxanthones are much more

easily nitrated than xanthone itself under the same conditions. Whereas xanthone gives only dinitroxanthones, 1- and 4-nitroxanthone give tetranitroxanthones, and 2- and 3-nitroxanthone give trinitroxanthones. As many as six tetranitroxanthones have been prepared from lower nitroxanthones with very great ease. The orientation of these tetranitro-compounds is still under investigation, but they have been distinguished from each other mainly by their bromination products. By this method it has been found that the α_1- and β_1-tetranitro-compounds are identical, and two of their nitro-groups are so stable that they are not removed by bromine, even when heated at 300° for twenty-six hours (this vol., p. 995).

Further nitration of some of these tetranitroxanthones (α_1-, α_2-, and β_2-) has been attempted by boiling them with mixtures of sulphuric acid and fuming nitric acid in various proportions, but without success.

A New Heterocyclic Type.

Skraup's reaction was utilised by F. Mayer (*Ber.*, 1909, **42**, 3064) in order to fuse a pyridine ring on to a thioxanthone nucleus. He obtained thereby one thioxanthoquinoline from 2-aminothioxanthone, but he neither studied this compound thoroughly nor extended this reaction to any other member of the thioxanthone or xanthone series. It was therefore proposed to study this reaction, particularly in the xanthone series, with the expectation of obtaining a series of tetracyclic compounds where one pyridine ring would be united with a pyrone ring together with two benzene rings:



It will be seen that the pyrone ring is protected on both sides by benzene rings, whereas the pyridine ring is protected only on one side. Accordingly, the respective stability of these pyrone and pyridine rings can be usefully studied.

It has been found, as expected, that an aminoxanthone, when treated with glycerol and sulphuric acid, gives a heterocyclic compound exactly of the type represented above. The reaction takes place with such great readiness that it is sufficient to use the nitro- instead of the amino-derivative. This naturally simplifies the synthesis considerably, and Dey and Goswami (T., 1919, **115**, 531) have noticed the same fact in similar syntheses in the coumarin series. In this way, β-dinitroxanthone gives *nitroxanthoquinoline*. The utilisation of the other nitro-group for fusing another pyridine ring to the already existing tetracyclic nucleus, as well as the synthesis of this type of tetracyclic compounds from other nitro-derivatives of xanthone, are under investigation.

Action of Sodium Methoxide on Nitroxanthones.

One remarkable reaction of the nitroanthraquinones is the ease with which a nitro-group is displaced by a methoxy-group. All the known dinitroanthraquinones have been converted into their corresponding dimethoxy-compounds by boiling them with sodium methoxide. Although xanthone behaves like anthraquinone in many important reactions, it differs entirely in this particular case. None of the nitro-groups of α- or β-dinitroxanthone is displaced by a methoxy-group when treated with sodium methoxide, but the corresponding nitroxanthhydrols are produced. These substances dissolve in alkali hydroxide as well as in concentrated acids with distinctive colours.

	Colour in solutions of				
Substance.	NaOH.	H_2SO_4.	HCl.	HNO_3.	$CH_3{\cdot}CO_2H$.
α-Dinitroxanthhydrol	Yellow	Deep yellow	Yellow	Pink	Orange-red
β-Dinitroxanthhydrol	,,	,,	Pale yellow	—	—

Although xanthhydrol is quickly converted into an ether, these dinitroxanthhydrols do not undergo this reaction, perhaps because of the influence of the nitro-groups. When boiled with mild oxidising agents, they are converted into the original nitroxanthones.

Halogenation.

Three different methods have been employed for the preparation of halogen derivatives of xanthone, namely: (1) direct halogenation; (2) synthesis according to Ullmann's method (*Annalen*, 1907, **355**, 359), and (3) direct displacement of the nitro-group by halogen.

Chloroxanthones.

2-Chloroxanthone was prepared by Ullmann (*loc. cit.*; compare Ullmann and Wagner, *Annalen*, 1910, **371**, 388) while studying the condensation of *o*-chlorobenzoic acid and its derivatives with phenol, 3-chloroxanthone was synthesised by Gomberg and Cone (*Annalen*, 1909, **370**, 142) by a similar method, and octachloroxanthone was prepared by Steiner (*Monatsh.*, 1915, **36**, 175) whilst studying the chlorination of cyclic ketones by means of antimony pentachloride. It is proposed to study the chlorination of xanthone systematically by all the three methods mentioned above, but at present attention has mainly been confined to the second method, by which all the possible isomeric monochloroxanthones have been synthesised.

Chlorination.—The direct chlorination of xanthone has not yet been carried out systematically, and the only method that has been tried is by dissolving xanthone in acetic acid and passing chlorine into the solution, using a trace of iodine as a catalyst. The products are 3-chloroxanthone and a *dichloroxanthone*; the latter can easily be obtained pure, but it is very difficult to remove the last traces of it from the former.

Ullmann's Synthesis.—Of the four possible monochloroxanthones, 2- and 3-chloroxanthone were synthesised by Ullmann and by Gomberg and Cone respectively (*loc. cit.*). The other two isomerides have now been prepared.

Bromoxanthones.

Bromination.—When xanthone in acetic acid solution is heated with one molecule of bromine and a trace of iodine, 3-bromoxanthone is obtained (Dhar, T., 1916, **109**, 745; compare *Annalen*, 1909, **370**, 142), but when concentrated sulphuric acid is used as a solvent instead of acetic acid, the product is 2-bromoxanthone. Each of these bromo-compounds when heated with bromine passes easily into the same dibromo-derivative, and therefore when a slight excess of bromine is used in the preparation of a monobromo-compound, dibromoxanthone is always formed. This is the main product of the direct bromination of xanthone when the operation is carried on under different conditions and with different catalysts. One striking fact in connexion with the direct bromination of xanthone is that although xanthone is brominated in sulphuric acid solution by liquid bromine, it is not attacked by a mixture of potassium bromide and potassium bromate in sulphuric acid solution.

Synthesis.—2-Bromoxanthone has also been synthesised from *o*-chlorobenzoic acid and *p*-bromophenol, and 4-bromoxanthone has been obtained by a similar method.

Direct Displacement of Nitro-group by Bromine.—By this method, several bromoxanthones have been prepared. The method serves as the only means of preparing certain bromo-derivatives, and there is a remarkable economy of bromine as the whole amount of bromine enters the nucleus.

Experimental.

Xanthone.

One hundred grams of salicylic acid when boiled with 100 grams of acetic anhydride and distilled gave only 20 grams of xanthone (compare Graebe, *Annalen*, 1889, **254**, 280). The yield was not improved by an increase in the amount of acetic anhydride or by extending the period of heating, nor was it affected appreciably when different samples of the materials were used. It was, however, raised to 40 per cent. of the salicylic acid used by the addition of a molecular proportion of phenol to the mixture. Thus a mixture of 50 grams of salicylic acid and 50 grams of phenol, when boiled for six hours with 100 grams of acetic anhydride and distilled, yielded 20 grams of xanthone. In all these cases the yield is extremely poor when no acetic anhydride is employed, and acetic acid has no effect at all.

When *o*-acetoxybenzoic acid is similarly boiled either alone or with acetic anhydride, it yields xanthone equivalent to 20 per cent. of its salicylic acid content.

Mononitroxanthones.

1-*Nitroxanthone.*—*m*-Nitrophenol (1·6 grams) was dissolved in 20 c.c. of methyl alcohol containing 0·4 gram of sodium. *o*-Chlorobenzoic acid (1·5 grams) was then added to the solution, and also a trace of copper powder. The alcohol was evaporated, and the dry, brown substance began to soften at about 100°; the temperature of the bath was raised to 110°, when the contents of the vessel melted to a dark brown liquid which solidified partly at about 140°. When cool, the contents were powdered and heated on a steam-bath for ten minutes with 15 c.c. of concentrated sulphuric acid. The solution was cooled, poured into water, and the precipitate collected. The substance crystallised from alcohol in slender, brown needles melting at 210° (Found: N = 5·99. $C_{13}H_7O_4N$ requires N = 5·80 per cent.).

It shows no fluorescence in concentrated sulphuric acid solution, but gives a yellow colour only.

2-*Nitroxanthone.*—*p*-Nitrophenol (4·2 grams) was dissolved in 20 c.c. of methyl alcohol, and 0·7 gram of metallic sodium was then added to the solution. When it was clear, 4·7 grams of *o*-chlorobenzoic acid were added, and a trace of copper powder was introduced as a catalyst. The alcohol was evaporated off slowly, and then the temperature of the bath was raised very slowly to 140°, when the orange-brown, hard mass melted to a viscid liquid of the same colour. After some twenty minutes, the colour began to change, and the liquid then became converted into a greyish-red, jelly-like substance. The temperature was very cautiously raised to 160°, when the dark-coloured substance solidified. The whole mass, however, bursts into flame at about this temperature if more than one atomic proportion of sodium is taken or if the temperature is raised suddenly. The substance, when cool, was powdered and heated on a steam-bath with 50 c.c. of concentrated sulphuric acid for twenty-five minutes. The solution, when cool, was poured into water, and the precipitate was collected (7 grams). The substance crystallised from alcohol in slender, brown needles melting at 200° and dissolving in sulphuric acid with a greenish-blue fluorescence (Found: N=5·56. $C_{13}H_7O_4N$ requires N=5·80 per cent.).

3-*Nitroxanthone.*—This was first prepared by Ullmann (*loc. cit.*) by the condensation of 2-chloro-4-nitrobenzoic acid with phenol. It has, however, been possible to obtain this compound directly from xanthone by nitration in the following way. Six grams of xanthone were dissolved in 12 c.c. of concentrated sulphuric acid, and 1·4 c.c. of nitric acid (D 1·500) added with shaking. Much heat was developed. The solution was kept overnight and then poured into water, the precipitate (about 7 grams) being collected and washed with water. About 2 grams of the substance, which did not dissolve in alcohol, consisted of β-dinitroxanthone. From the alcoholic solution, yellowish-white needles were obtained, which were found to contain traces of xanthone. The nitro-compound was purified by further crystallisation from alcohol. Traces of xanthone were found still to be associated with it, and could be removed only with very great difficulty, because of the almost equal solubility of each of these compounds in alcohol.

On reduction, traces of xanthone were removed, as this is insoluble in dilute hydrochloric acid, whereas the amino-compound was obtained as hydrochloride in the solution. The free amino-compound, isolated by precipitation with ammonia, melts at 232° (as given by Ullmann, *loc. cit.*).

When 1 gram of 3-nitroxanthone is dissolved in 10 c.c. of con-

centrated sulphuric acid and 5 c.c. of nitric acid (D 1·42) are added to the solution and the mixture kept overnight, a trinitroxanthone is obtained. This compound is described subsequently.

3-Nitroxanthone dissolves in sulphuric acid with a blue fluorescence much stronger than that shown by xanthone itself.

4-Nitroxanthone.—A mixture of 50 grams of salicylic acid and 50 grams of *o*-nitrophenol was boiled with 100 grams of acetic anhydride for ten hours and then distilled. Some tarry matter passed over at a very high temperature. This was boiled with alcohol with the addition of animal charcoal, and from the filtrate about 2·5 grams of yellow needles were obtained melting at 127° (Found: N = 5·71. $C_{13}H_7O_4N$ requires N = 5·80 per cent.). The compound dissolves in sulphuric acid with a green colour and without fluorescence. It is remarkable that no xanthone could be traced in the distillate. Attempts were made to condense *o*-nitrophenol with *o*-chlorobenzoic acid by Ullmann's method, but without success.

Dinitroxanthones.

α- and β-Dinitroxanthones are ordinarily obtained by nitrating xanthone with a mixture of nitric and sulphuric acids. They have also been prepared by nitrating xanthone with fuming nitric acid alone.

When 2 grams of xanthone are dissolved in 5 c.c. of nitric acid (D 1·500) and the solution is heated on a water-bath for about ten minutes, fine needles of β(or 2:7)-dinitroxanthone precipitate, and from the solution α-dinitroxanthone is obtained by precipitation with water and purification with nitric acid. Similar results are obtained with weaker nitric acid (D 1·42), but the quantity of acid should be proportionately greater, namely, 10 c.c. for each gram of xanthone, and the mixture should be heated for about three hours.

β(or 2:7)-*Dinitroxanthone.*—One gram of 2-nitroxanthone was dissolved in a cold mixture of 25 c.c. of nitric acid (D 1·42) and 25 c.c. of concentrated sulphuric acid. The solution was kept overnight, and then poured into water. The yellow precipitate (1·5 grams) was collected and crystallised from nitric acid, when it was obtained in white needles melting at 254°. When mixed with 2:7-dinitroxanthone (m. p. 262°), it melted at 254—260° (Found: N = 9·79. Calc.: N = 9·81 per cent.). From the nitric acid filtrate a trinitroxanthone was obtained (see below).

2:4-*Dinitroxanthone.*—This compound was prepared by Mayer (*loc. cit.*) by the condensation of sodium phenoxide and 2-chloro-3:5-dinitrobenzoic acid. It can also be prepared by condensing 2:4-dinitrophenol with *o*-chlorobenzoic acid in the following way.

2:4-Dinitrophenol (1·25 grams) and sodium (0·17 gram) are dissolved in methyl alcohol (20 c.c.), and to the clear solution *o*-chlorobenzoic acid (1·2 grams) and a trace of copper powder added. After evaporating the alcohol, the yellow residue melts partly at 160° and solidifies in a few minutes. It is cooled, powdered, and heated again to 160°, when it melts and resolidifies as before. This process is repeated about ten times, when the condensation is complete, and the substance does not melt on heating to 160°. If the temperature of the bath is raised with the view of completing the reaction in one operation, the whole mass suddenly inflames at about 200° without melting. After the completion of the condensation, the powdered substance is heated on a steam-bath with 20 c.c. of concentrated sulphuric acid for fifteen minutes. When cool, the solution is poured into water and the precipitate is collected. The substance, when decolorised with animal charcoal in alcoholic solution, crystallises from this solvent in yellow needles melting at 206° (Found: N = 9·91. Calc.: N = 9·81 per cent.).

Trinitroxanthones.

2:3:7-*Trinitroxanthone.*—When 2-nitroxanthone was nitrated (see above), 2:7-dinitroxanthone was the first product, and from the nitric acid filtrate a yellowish-white precipitate was obtained by adding water. After being boiled with alcohol to remove impurities, it melted at 205° (Found: N = 12·74. $C_{13}H_5O_8N_3$ requires N = 12·63 per cent.). The same trinitroxanthone was obtained when 6 grams of 2:7-dinitroxanthone were dissolved in 50 c.c. of concentrated sulphuric acid, 1·2 c.c. of nitric acid (D 1·500) added, and the solution was heated on a water-bath for twenty-four hours. The unchanged dinitro-compound was crystallised from nitric acid and collected, and the filtrate on concentration gave yellow needles melting at 205°.

This compound was also obtained by nitrating 3-nitroxanthone.

Dinitromonoaminoxanthone.—The trinitro-compound was reduced with alcoholic ammonium sulphide, and the product separated from alcohol as a dark brown powder melting and decomposing at 230° (Found: N = 14·55. $C_{13}H_7O_6N_3$ requires N = 14·43 per cent.).

Dinitroxanthoneazo-β-naphthol.—The dinitroaminoxanthone was diazotised in the usual way and coupled with β-naphthol. The azo-compound separates from alcohol as a dark red, amorphous powder melting at 270° (Found: N = 12·25. $C_{23}H_{12}O_7N_4$ requires N = 12·28 per cent.).

Trinitroxanthone.—Two grams of xanthone were dissolved in 7 c.c. of concentrated sulphuric acid with the aid of heat, and 2 c.c. of nitric acid (D 1·500) added to the cooled solution. The latter was then kept over the steam-bath, when a copious precipitate appeared in a few minutes consisting of yellow, glistening needles, which were filtered through asbestos and washed with dilute nitric acid, and finally with water. The substance dissolves freely in cold nitric acid (D 1·42). It melts at 225°, and is not identical with the trinitro-compound previously mentioned (Found: N=12·72. $C_{13}H_5O_8N_3$ requires N=12·63 per cent.).

Dinitromonoaminoxanthone.—This was obtained by reducing the trinitro-derivative with alcoholic ammonium sulphide in the usual way. It was obtained as a yellow powder melting at 290° (Found: N=14·47. $C_{13}H_7O_6N_3$ requires N=14·43 per cent.).

Tetranitroxanthones.

1-*Tetranitroxanthone.*—This compound was obtained by dissolving 0·5 gram of 1-nitroxanthone in 5 c.c. of concentrated sulphuric acid and adding 2·5 c.c. of nitric acid (D 1·42). The solution, on keeping overnight, deposited yellowish-white needles melting at 250°. It is evidently different from α_1-, α_2-, or β_2-tetranitroxanthones, which do not melt at 300° (Found: N=14·64. $C_{13}H_4O_{10}N_4$ requires N=14·89 per cent.).

4$_1$-*Tetranitroxanthone.*—Half a gram of 4-nitroxanthone was dissolved in 5 c.c. of concentrated sulphuric acid, and 2·5 c.c. of nitric acid (D 1·42) were then added gradually with shaking. At the first addition of nitric acid a violent reaction ensued, and the reaction vessel was cooled. After keeping the mixture for a few days, a reddish-yellow precipitate was obtained, which did not melt at 300° (Found: N=15·32. $C_{13}H_4O_{10}N_4$ requires N=14·89 per cent.).

4$_2$-*Tetranitroxanthone.*—When the filtrate from the nitro-compound described above was added to water, there was obtained a brown powder, which could not be crystallised from alcohol, benzene, or nitric acid. It melts and decomposes at 200° (Found: N=14·70. $C_{13}H_4O_{10}N_4$ requires N=14·89 per cent.).

α_1-*Tetranitroxanthone.*—Thirteen grams of α-dinitroxanthone were added to a mixture of 150 c.c. of concentrated sulphuric acid and 150 c.c. of nitric acid (D 1·42). The mixture was heated on a steam-bath, when a clear solution was obtained in a few minutes and shining, yellowish-white crystals (10·7 grams) separated in about six hours. These did not melt at 300° (Found: N=14·79. $C_{13}H_4O_{10}N_4$ requires N=14·89 per cent.). This substance when

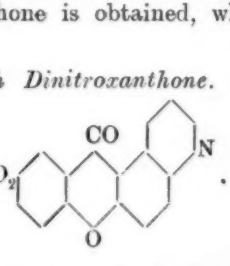
heated with bromine and a trace of iodine in a sealed tube gives dibromodinitroxanthone (m. p. 265°) (see this vol., pp. 998—999).

α_2-Tetranitroxanthone.—From the filtrate from the preceding compound, crystals, in the form of broken plates, were obtained by adding water. They also do not melt at 300° (Found: N = 14·69. $C_{13}H_4O_{10}N_4$ requires N = 14·89 per cent.).

This substance, when treated similarly with bromine, gives a tetrabromoxanthone (m. p. 255°).

β_2-Tetranitroxanthone.—Ten grams of 2:7-dinitroxanthone were added to a mixture of 150 c.c. of concentrated sulphuric acid and 150 c.c. of nitric acid (D 1·42). The mixture was heated for about six hours, when bright yellowish-white crystals (9 grams) were precipitated. The compound was found to be identical with α_1-tetranitroxanthone, as both these substances gave the same dibromodinitroxanthone when treated similarly with bromine. From the filtrate, 3·5 grams of shining, white, broken plates were obtained, which did not melt at 300° (Found: N = 14·69. $C_{13}H_4O_{10}N_4$ requires N = 14·89 per cent.). When this substance is heated with bromine exactly in the same way as the other tetranitro-compounds, a hexabromoxanthone is obtained, which melts at 285°.

Skraup's Synthesis with Dinitroxanthone.

Nitroxanthoquinoline, 

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Three grams of 2:7-dinitroxanthone were dissolved in 5 c.c. of concentrated sulphuric acid, and 12 c.c. of glycerol added. The addition of the latter precipitated the nitro-compound. The mixture was heated in a paraffin-bath, and at about 140° it began to froth, when the flask was shaken and the temperature lowered to 110°. Heating was continued for four hours at about 120°, and then for a further two hours at about 140°, when a semi-solid mass resulted. This was then heated for a further three hours until the black mixture became solid. The mass was powdered, and the crude product boiled with water and filtered. The filtrate, on being rendered alkaline, gave an orange-red, colloidal precipitate, which settled on keeping overnight and was collected. The substance separates from alcohol as an orange-red powder, which sinters at 200° and melts at 205—210° (Found: N = 9·75. $C_{16}H_8O_4N_2$ requires N = 9·59 per cent.). The substance dissolves readily in alcohol, acids, or excess of alkali hydroxide.

Xanthhydrols.

α-Dinitroxanthhydrol.—α-Dinitroxanthone (2·5 grams) was suspended in 100 c.c. of methyl alcohol, and 1 gram of sodium added in small pieces with shaking. The colour of the mixture became first orange, and finally deep red. It was boiled under reflux for half an hour, when a clear, dark red solution was obtained; the boiling was continued for a further period of one and a-half hours, and the solution filtered hot. A yellowish-brown precipitate was obtained on acidifying the solution with hydrochloric acid, and this crystallised from acetic acid in brown needles melting at 185° (Found: N = 10·11. $C_{13}H_8O_6N_2$ requires N = 9·72 per cent.). The substance dissolves in alcohol and in cold dilute alkali hydroxide, in the latter solvent with a yellow colour. Its solution in concentrated sulphuric or hydrochloric acid is pale yellow, and in nitric acid it dissolves with a pink coloration. When heated with glacial acetic acid, it dissolves to an orange-red solution.

β(or 2:7)-*Dinitroxanthhydrol.*—This substance was obtained by treating 2·5 grams of 2:7-dinitroxanthone with sodium and methyl alcohol, as in the case of the α-dinitro-compound. It crystallised from alcohol in slender, yellowish-white needles melting and decomposing at 196° (Found: N = 9·65. $C_{13}H_8O_6N_2$ requires N = 9·72 per cent.). The substance dissolves in cold aqueous alkali hydroxide as well as in concentrated sulphuric acid with a yellow coloration, and in concentrated hydrochloric acid to a pale yellow solution.

Each of these dinitroxanthhydrols, when boiled with a mild oxidising agent, such as a dilute solution of hydrogen peroxide or potassium permanganate, is converted into the corresponding dinitroxanthone.

Chloroxanthones.

1-*Chloroxanthone.*—*o*-Chlorobenzoic acid (1·6 grams), *m*-chlorophenol (1·4 grams), and sodium (0·4 gram) were dissolved in methyl alcohol (10 c.c.), a trace of copper powder being added as a catalyst. The solution was heated on an oil-bath, and the alcohol evaporated, when the substance melted at about 200° and solidified at about 215°. It was cooled, powdered, and heated on a steam-bath with 15 c.c. of concentrated sulphuric acid for fifteen minutes. When cool, the solution was poured into water, and the precipitate collected. The substance crystallised from aqueous alcohol in white needles melting at 100°. It dissolves in sulphuric acid with a green fluorescence. In this synthesis, either 1-chloro-

xanthone or 3-chloroxanthone or both may possibly be formed, but only one product was obtained. As it differed from 3-chloroxanthone, which melts at 130°, it must be 1-*chloroxanthone* (Found: Cl = 15·46. $C_{13}H_7O_2Cl$ requires Cl = 15·40 per cent.).

1-*Anilinoxanthone*.—One gram of the substance described above was boiled with 3 c.c. of aniline and a trace of copper powder for six hours. A blue precipitate was obtained by pouring the solution into water acidified with hydrochloric acid. After being purified by extraction with alcohol, it melted at 120—125° (Found: N = 4·86. $C_{19}H_{13}O_2N$ requires N = 4·87 per cent.).

1-*Chlorotetranitroxanthone*.—Half a gram of 1-chloroxanthone was dissolved in 7 c.c. of concentrated sulphuric acid, and 5 c.c. of nitric acid (D 1·42) were added to the solution with shaking. The solution was kept overnight, when white needles were obtained, which melted at 195° (Found: N = 13·70. $C_{13}H_2O_{10}N_4Cl$ requires N = 13·69 per cent.). From the filtrate, a white precipitate was obtained, which was too small in amount for any detailed examination.

2-*Chloroxanthone*.—*p*-Chlorophenol (1·4 grams) was dissolved in methyl alcohol (10 c.c.), and sodium (0·4 gram) and *o*-chlorobenzoic acid (1·6 grams) and a trace of copper powder were added to the solution. The alcohol was evaporated, and the viscous, semi-solid mass was heated to 140°, and kept at that temperature for half an hour, when it darkened. It dried to a black solid mass at 150°. The temperature was further raised to 200°, and then the substance was cooled, powdered, and heated on a water-bath with 15 c.c. of concentrated sulphuric acid for fifteen minutes. When cool, the solution was poured into water; the precipitate was collected, crystallised from alcohol, and obtained in white needles melting at 165° (Ullmann, *loc. cit.*, gives 171°). It dissolves in sulphuric acid with a blue fluorescence (Found: Cl = 15·72. Calc.: Cl = 15·40 per cent.).

2-*Chlorotetranitroxanthone*.—This compound was obtained by nitrating 2-chloroxanthone with concentrated sulphuric and nitric acids. For each gram of substance, 10 c.c. of sulphuric acid and 7 c.c. of nitric acid were used. The substance was obtained in slender, yellowish-white needles melting at 205° (Found: N = 13·75. $C_{13}H_3O_{10}N_4Cl$ requires N = 13·69 per cent.).

4-*Chloroxanthone*.—This substance was obtained by the condensation of *o*-chlorobenzoic acid with *o*-chlorophenol in the manner described in the syntheses of 1-chloroxanthone. It crystallised from alcohol in slender, white needles melting at 130°. It dissolves in concentrated sulphuric acid with a green fluorescence (Found: Cl = 15·36. $C_{13}H_7O_2Cl$ requires Cl = 15·40 per cent.).

4-*Chlorotrinitroxanthone*.—This compound was obtained by

nitrating 4-chloroxanthone with concentrated sulphuric and nitric acids. For each gram of the substance, 5 c.c. of sulphuric acid and 4 c.c. of nitric acid were used. Brownish-yellow needles were obtained on keeping the reaction mixture overnight. The substance melts at 235° (Found: N = 11·14. $C_{13}H_4O_8N_3Cl$ requires N = 11·49 per cent.).

4-Chlorodinitroxanthone.—This substance was obtained from the filtrate of the trinitro-compound as a pale yellow powder melting and decomposing at 195—200° (Found: N = 8·81. $C_{13}H_5O_6N_2Cl$ requires N = 8·73 per cent.).

Dichloroxanthone.—Xanthone (7·5 grams) was dissolved in acetic acid (50 c.c.) with the aid of heat. A current of dry chlorine was passed into the solution, which was kept warm by heating the reaction vessel over a steam-bath until approximately one molecular proportion of chlorine was absorbed. A trace of iodine was used as a catalyst. The product (10 grams) crystallised from alcohol in slender, white needles melting at 225° (Found: Cl = 26·86. $C_{13}H_6O_2Cl_2$ requires Cl = 26·80 per cent.). The substance dissolves in concentrated sulphuric acid with a strong green fluorescence. From the alcoholic filtrate from the dichloroxanthone another product mixed with it was obtained, which appeared to be 3-chloroxanthone from its melting point and chlorine content, but it has not yet been possible to purify it completely.

Dichlorodinitroxanthone.—The dichloro-compound was nitrated in the cold with a mixture of equal volumes of nitric (D 1·42) and concentrated sulphuric acids (100 c.c. for each gram of the substance). On keeping the solution overnight, yellow needles were obtained, which melted at 240° (Found: N = 8·10. $C_{13}H_4O_6N_2Cl_2$ requires N = 7·88 per cent.).

Bromoxanthones.

2-Bromoxanthone.—*p*-Bromophenol (2·5 grams) and sodium (0·6 gram) were dissolved in methyl alcohol (15 c.c.) and *o*-chlorobenzoic acid (2·3 grams) and a trace of copper powder were added to the solution. It was heated to 160°, when a hard, black mass was obtained. The temperature was raised to 220°, but the substance did not fuse. It was cooled, powdered, and heated over a steam-bath with 25 c.c. of concentrated sulphuric acid for twenty-five minutes. When cool, the solution was poured into water and the precipitate collected. It crystallised from aqueous alcohol in brown needles melting at 150°, and dissolved in sulphuric acid with a yellow colour, but no fluorescence (Found: Br = 29·00. $C_{13}H_7O_2Br$ requires Br = 29·16 per cent.). 2-Bromoxanthone is also obtained when xanthone is brominated in concentrated

sulphuric acid solution with bromine and a trace of iodine. It is very difficult, however, to isolate the substance in a pure condition, because the last traces of either xanthone or dibromoxanthone, which are always associated with this compound, cannot easily be removed.

2-*Bromo-α-tetranitroxanthone*.—2-Bromoxanthone (0·7 gram) was dissolved in concentrated sulphuric acid (10 c.c.), and nitric acid (5 c.c. of D 1·42) then added gradually to the solution with shaking. No precipitate was formed after keeping it for a few days. The solution was poured into water, and the precipitate was boiled with alcohol, in which it partly dissolved. From the alcoholic solution, the substance was obtained in slender, brown needles melting at 210° (Found: N = 12·02. $C_{13}H_3O_{10}N_4Br$ requires N = 12·31 per cent.).

2-*Bromo-β-tetranitroxanthone*.—The residue of the nitro-compound described above was dissolved in benzene, and crystallised from this solution in brown needles melting at 270° (Found: N = 12·21. $C_{13}H_3O_{10}N_4Br$ requires N = 12·31 per cent.). When 2-bromoxanthone was heated with bromine (1 or 2 mols.) in acetic acid solution and a trace of iodine, over a sand-bath, a dibromo-compound was obtained which melted at 212°. This compound was identified as 2:7-dibromoxanthone by the method of mixed melting points. It is also obtained by brominating xanthone with bromine, using iron filings as a catalyst.

4-*Bromoxanthone*.—This compound was obtained by condensing *o*-bromophenol with *o*-chlorobenzoic acid in the usual way. It crystallised from alcohol in greyish-white needles melting at 140°. It shows no fluorescence in sulphuric acid solution (Found: Br = 29·28. $C_{13}H_7O_2Br$ requires Br = 29·16 per cent.).

4-*Bromodinitroxanthone*.—4-Bromoxanthone was dissolved in the requisite amount of concentrated sulphuric acid in the cold, and nitric acid (D 1·42) was added to the solution (20 c.c. for each gram of the substance). On keeping the solution overnight, yellowish-white needles were obtained, which melted at 295° (Found: N = 8·09. $C_{13}H_5O_6N_2Br$ requires N = 7·67 per cent.).

The author takes this opportunity of expressing his thanks to Professor J. F. Thorpe and Dr. M. A. Whiteley for their kind encouragement, and to the Van't Hoff Memorial Fund Committee and to the Chemical Society for Research Grants which met part of the expenses.

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CXIX.—*Complex Metallic Ammines. Part IV.* cis-*Sulphoacetato-*, cis-*Methionato- and* cis-*Dimethylmalonato-diethylenediaminecobaltic Salts.*

By Thomas Slater Price and James Cooper Duff.

Werner (*Annalen*, 1911, **386**, 79) has shown that complex cobaltammines containing the malonato-radicle are easily prepared, but he was of the opinion (*ibid.*, pp. 26, 81) that complexes containing a higher number of atoms to the ring than six could not be obtained. Price and Brazier (T., 1915, **107**, 1367) showed, however, that when a sulphur atom forms one of the components of the ring, an eight-ring can be obtained, and were successful in preparing *cis*-sulphonyldiacetatodiethylenediaminecobaltic salts. The part played by the sulphur in enabling such compounds to be isolated is not clear. It may be that the presence of sulphur in the acid radicle enabled ring-formation to take place readily, or it may be that the compounds could be isolated, because they were readily obtained in the crystalline form, whereas the attempts by Werner to obtain products containing the succinato- and other radicles only gave rise to uncrystallisable syrups or glasses. It was therefore of interest to investigate the behaviour of other dibasic acids containing sulphur, and the present communication details the results obtained with sulphoacetic acid,

$$SO_3H\cdot CH_2\cdot CO_2H,$$

and with methionic acid, $CH_2(SO_3H)_2$, both of which give rise to crystalline compounds.

In a previous paper (Price and Brazier, T., 1915, **107**, 1713) it has been shown that malonic acid forms an additive compound with dichlorodiethylenediaminecobaltic hydrogen malonate, namely, $[Cl_2Co\,en_2]HA,H_2A$, where $H_2A=CH_2(CO_2H)_2$, but that the substituted malonic acids do not give rise to such additive compounds, and a tentative explanation of the results obtained was advanced. It was therefore of interest to ascertain whether the substituted malonic acid residue could be introduced into the cobalt complex, giving compounds similar to the malonato-compounds, or whether some such steric hindrance as is postulated in the aforementioned paper prevented their formation. The first experiments were made with dimethylmalonic acid, and we have been successful in preparing dimethylmalonatodiethylenediaminecobaltic salts. The other substituted malonic acids have not yet been investigated, but owing to the fact that one of us (T.S.P.) is taking up other duties, it is considered advisable to publish the results hitherto obtained.*

* These researches are being continued by Mr. Duff (T.S.P.).

The fact that the dimethylmalonic acid residue can be introduced into the nucleus does not necessarily invalidate the explanation given previously of the formation of additive compounds, since, as will be seen in the experimental part, a higher temperature than the ordinary was used, whereby the formation of a ring complex may be greatly facilitated.

As will be seen later, sulphoacetic and methionic acids do not form additive compounds with their dichlorodiethylenediaminecobaltic acid salts, thus differing markedly from their analogue, malonic acid. No explanation of this is offered at present, since further work is necessary.

Experimental.

cis-Sulphoacetatodiethylenediaminecobaltic Salts, YX, where

$$Y = \left[CH_2 \begin{matrix} SO_2 \cdot O \\ CO - O \end{matrix} > Co\ en_2 \right].$$

To obtain the *bromide*, YBr, 5 grams of carbonatodiethylenediaminecobaltic bromide were dissolved in 80 c.c. of warm water, and a solution of 2·19 grams of sulphoacetic acid in 20 c.c. of water was added. Evaporation of the mixed solution on the water-bath to a small bulk only resulted in a very poor yield of crystals. It was found best to heat the solution, after the evolution of carbon dioxide had slackened, in a closed bottle at 105° for four hours, and then evaporate to small bulk on the water-bath. After remaining in the ice-chest overnight, the anhydrous bromide separated in small, carmine-red plates, which were collected and washed with water and alcohol. The yield was 2·4 grams, but a further small quantity was obtained by evaporation of the filtrate (Found: Co = 14·87; Br = 20·08. $C_6H_{18}O_5N_4BrSCo$ requires Co = 14·85; Br = 20·15 per cent.).

The *nitrate*, YNO_3, was obtained in brick-red, elongated plates by precipitating a solution of 2 grams of the bromide in 50 c.c. of water with the equivalent quantity (0·86 gram) of silver nitrate. After shaking for one hour, the silver bromide was collected and the filtrate evaporated to low bulk on the water-bath. The crystals of the nitrate separated slowly on keeping in the ice-chest. Yield, 0·8 gram (Found: Co = 15·39; N = 18·24. $C_6H_{18}O_8N_5SCo$ requires Co = 15·56; N = 18·47 per cent.).

The *thiocyanate*, YSCN, was obtained by adding 1·5 grams of solid potassium thiocyanate to a saturated solution containing 3 grams of the bromide. The potassium thiocyanate dissolved, and, after leaving overnight in the ice-chest, microscopic, brick-red crystals of the complex thiocyanate separated (Found: Co = 15·62;

N=18·91. $C_7H_{18}O_5N_5S_2Co$ requires Co=15·73; N=18·67 per cent.).

The *platinichloride*, Y_2PtCl_6, was prepared by filtering a saturated solution containing 2 grams of the bromide into a 5 per cent. solution of chloroplatinic acid. Microscopic, pale brown crystals slowly separated; these were collected after two hours and washed with alcohol and ether, and dried in a vacuum desiccator [Found: Co=11·11; Pt=18·95. $(C_6H_{18}O_5N_4SCo)_2PtCl_6$ requires Co=11·32; Pt=18·72 per cent.].

The *hydrogen sulphoacetate*, $YSO_3{\cdot}CH_2{\cdot}CO_2H$, was obtained by dissolving 6 grams of the carbonato-bromide in 120 c.c. of water and shaking the cooled solution with 4 grams of freshly prepared moist silver oxide for half an hour. The product was then filtered into an aqueous solution of 5·25 grams of sulphoacetic acid, the proportions being two molecules of the acid to one of the carbonato-base. The resulting solution was evaporated to low bulk on the water-bath, and, after keeping overnight in the ice-chest, deposited microscopic, pink crystals, which dissolve readily in cold water. Yield, 2·8 grams (Found: Co=12·79; N=12·33. $C_8H_{21}O_{10}N_4S_2Co$ requires Co=12·93; N=12·28 per cent.).

cis-Methionatodiethylenediaminecobaltic Salts, YX, where

$$Y=\left[CH_2\begin{matrix}SO_2{\cdot}O\\SO_2{\cdot}O\end{matrix}>Co\ en_2\right].$$

The *bromide*, $YBr,2H_2O$, was only obtained after several attempts had been made to prepare it from the carbonato-bromide according to the method used by Price and Brazier in making sulphonyldiacetatodiethylenediaminecobaltic bromide (*loc. cit.*). It was found that on mixing solutions of the carbonato-bromide and methionic acid in equivalent quantities and evaporating on the water-bath, pink, microscopic crystals separated in increasing quantity as evaporation proceeded. These crystals, however, contained no bromine, and were later identified as the methionato-methionate (Found: Co=13·20). On further evaporation, the mother liquor gave no crystals of the bromide, a syrupy liquid resulting which contained some unused carbonato-bromide. To avoid this formation of the methionate, it was found best to dissolve 5 grams of the carbonato-bromide in 120 c.c. of water and add a solution of 2·73 grams of methionic acid in 40 c.c. of water. The whole solution was then well boiled for twenty minutes, keeping the volume at about 150 c.c. by the addition of boiling water.* After evaporating the resulting solution on the water-bath to low

* This method of treatment has already given successful results in the case of succinato-compounds, which will be dealt with in a later paper by one of us.

bulk and keeping for two days in the ice-chest, the pure methionato-bromide separated in purplish-red plates, which were collected and washed with water and alcohol. Yield, 1·4 grams [Found: Co=12·50; Br=17·02; S=13·28; H_2O (at 100°)=7·74. $C_5H_{18}O_6N_4BrS_2Co,2H_2O$ requires Co=12·57; Br=17·04; S=13·64; H_2O=7·68 per cent.].

The *nitrate*, $YNO_3,2H_2O$, was obtained by shaking for one hour a solution of 3 grams of the hydrated bromide in 60 c.c. of water with the equivalent quantity (1·08 grams) of silver nitrate. The silver bromide was then collected and the filtrate evaporated to low bulk on the water-bath. After keeping for several days in the ice-chest, the nitrate separated in carmine-red, elongated plates. Yield, 0·5 gram [Found: Co=13·42; N=15·76; H_2O (at 110°)=7·94. $C_5H_{18}O_9N_5S_2Co,2H_2O$ requires Co=13·08; N=15·52; H_2O=7·98 per cent.].

The *thiocyanate*, YSCN, was prepared by adding 1·5 grams of solid potassium thiocyanate to a saturated solution of 3 grams of the methionato-bromide. After keeping overnight, the complex thiocyanate separated in microscopic, dark red crystals (Found: Co=14·68; N=17·40. $C_6H_{18}O_6N_5S_3Co$ requires Co=14·35; N=17·03 per cent.).

The *platinichloride*, Y_2PtCl_6, was obtained by filtering a saturated solution of the methionato-bromide into a 5 per cent. solution of chloroplatinic acid. Microscopic, light brown crystals readily separated, which were washed with alcohol and ether and dried in a vacuum desiccator [Found: Co=10·34; Pt=17·83. $(C_5H_{18}O_6N_4S_2Co)_2PtCl_6$ requires Co=10·58; Pt=17·52 per cent.].

The hydrogen methionate could not be obtained, although the same method was used that has always been successful in similar cases. When two molecular proportions of methionic acid in solution were mixed with one of the carbonato-base, the crystals which separated on evaporation always proved to be the normal methionate. When this was dissolved in a boiling solution of methionic acid, only the unchanged salt separated on evaporation. The *normal methionate*, $CH_2(SO_3Y)_2$, was prepared by dissolving 7 grams (2 mols.) of the carbonato-bromide in 120 c.c. of warm water, shaking for half an hour with 3·8 grams of freshly prepared silver oxide, and filtering from the silver bromide into a solution containing 5·78 grams (3 mols.) of methionic acid. The mixed solution was then evaporated to low bulk on the water-bath. Complete separation of the normal methionate in pink, microscopic crystals only occurred when a little water was added to the resulting syrup and the whole well stirred. The yield was 7·3 grams. The salt is almost insoluble in cold water, but dis-

solves readily in hot water (Found: Co=13·56; N=12·64; S=21·37. $C_{11}H_{38}O_{18}N_8S_6Co_2$ requires Co=13·41; N=12·72; S=21·82 per cent.).

The normal methionate dissolves readily in cold dilute ammonia or sodium carbonate solution, but is not reprecipitated on acidifying. Barium hydroxide solution also dissolves it, giving a blood-red solution, from which barium methionate separates on keeping. Excess of barium hydroxide is required for solution, so that the reaction cannot be used as a method for obtaining the methionato-hydroxide, and hence the chloride. When the normal methionate is heated with a solution of barium chloride, a blood-red solution results, from which barium methionate separates on cooling. The filtrate from these crystals changes to a purple colour on evaporation, and small, purple crystals of *cis*-dichlorodiethylenediaminecobaltic chloride separate after a time (Found: Co=20·86. Calc.: Co=20·67 per cent.).

Concentrated solutions of the methionato-bromide do not give any precipitate when mixed with a solution of mercuric bromide in potassium bromide solution. On boiling the resulting solution, however, there is at once formed the green double salt of mercuric bromide and the *trans*-dibromo-bromide, $[Br_2Co\,en_2]Br,HgBr_2$, which separates from the hot solution in small, flattened needles (Found: Co=7·47; Br=49·83. Calc.: Co=7·56; Br=51·28 per cent.).

trans-*Dichlorodiethylenediaminecobaltic Salts.*

Since both sulphoacetic acid and methionic acid may be considered to be analogues of malonic acid, it was expected that they would give additive compounds with their acid salts of dichlorodiethylenediaminecobalt. This was found not to be the case, however, the substitution of $\cdot CO_2H$ by $\cdot SO_3H$ thus playing a part which requires further investigation. Price and Brazier (*loc. cit.*, p. 1737) found that sulphonyldiacetic acid, which contains an SO_2-group in place of one of the CH_2-groups of glutaric acid, did give rise to such additive compounds.

trans-*Dichlorodiethylenediaminecobaltic hydrogen sulphoacetate*, $[Cl_2Co\,en_2]SO_3\cdot CH_2\cdot CO_2H$, separates immediately as emerald-green, striated, and elongated plates when 3 grams of the *trans*-dichlorochloride are stirred into a cold solution of 4·3 grams of sulphoacetic acid in 15 c.c. of water. Yield, 3·1 grams (Found: Co=15·24; Cl=18·37. $C_6H_{19}O_5N_4Cl_2SCo$ requires Co=15·16; Cl=18·23 per cent.).

cis-Sulphoacetatodiethylenediaminecobaltic chloride could not be obtained from the above hydrogen sulphoacetate in the same way as oxalatodiethylenediaminecobaltic chloride was obtained from the

dichloro-hydrogen oxalate (Price and Brazier, *loc. cit.*, p. 1726). When a solution of the hydrogen sulphoacetate was boiled, the colour changed to the blood-red colour of a *cis*-salt, but on evaporation to small bulk, only green crystals could be separated. Repeated boiling of the solution and evaporation only resulted in the recovery of the green crystals of the unchanged hydrogen sulphoacetate.

trans-*Dichlorodiethylenediaminecobaltic methionate*, $[Cl_2Co\ en_2]_2(SO_3)_2CH_2$, separated in green, elongated plates when 3 grams of the *trans*-dichloro-chloride were stirred into a cold solution of 4·5 grams of methionic acid in 15 c.c. of water. The separation of crystals was complete after two hours in the ice-chest. Yield, 2·4 grams (Found: Co = 17·29; Cl = 20·81; S = 9·07. $C_9H_{34}O_6N_8Cl_4S_2Co_2$ requires Co = 17·50; Cl = 21·04; S = 9·49 per cent.).

When this salt was dissolved in water, together with a molecular proportion of methionic acid, and the solution boiled for fifteen minutes, the colour became deep red, but, on evaporating almost to dryness, only green crystals of the original substance separated. The acid salt could not be obtained.

cis-Dimethylmalonatodiethylenediaminecobaltic Salts, YX, where $Y = \left[CMe_2\langle\begin{matrix}CO\cdot O\\CO\cdot O\end{matrix}\rangle Co\ en_2\right]$.

Before commencing the preparation of these salts, the method described by Price and Brazier (*loc. cit.*, p. 1373) for the preparation of *cis*-sulphonyldiacetatodiethylenediaminecobaltic bromide was tested in the case of the malonato-bromide. This consisted in the preparation of the bromide directly by the interaction of one molecular proportion of the carbonato-bromide and one molecular proportion of malonic acid, whereas Werner's method of preparation of such compounds is first to prepare the carbonato-hydroxide and then add two molecular proportions of malonic acid. The method was found to be satisfactory, *cis-malonatodiethylenediaminecobaltic bromide*, $[CH_2(CO_2)_2Co\ en_2]Br,xH_2O$, being obtained in large, rhombic, dark red plates, which very readily effloresced on exposure to the air. A freshly prepared specimen, which had slightly effloresced, gave Co = 14·48, whereas $C_7H_{18}O_4N_4BrCo,xH_2O$ requires Co = 14·21 for $3H_2O$ and Co = 14·86 for $2H_2O$. The anhydrous substance gave Co = 16·25, theory requiring Co = 16·34 per cent. The corresponding thiocyanate, $C_8H_{18}O_4N_5SCo$, was readily obtained, and possessed the properties described by Werner (*Annalen*, 1911, **386**, 81) (Found: Co = 17·19. Calc.: Co = 17·39 per cent.).

To obtain cis-*dimethylmalonatodiethylenediaminecobaltic bromide*, $YBr,2H_2O$, 5 grams of the carbonato-bromide were dissolved in 80 c.c. of warm water and 2·07 grams (1 mol. equiv.) of dimethylmalonic acid added. The resulting solution was evaporated to low bulk on the water-bath, and, after keeping in the ice-chest overnight, crimson-red, microcrystalline plates of the desired salt separated in small quantity. Crystallisation, or, it may be, the introduction of the dimethylmalonato-residue into the complex, takes place very slowly, and it was necessary repeatedly to collect the crystals, wash with alcohol, and evaporate the filtrate and washings in order to obtain any quantity of the salt. The solution cannot be boiled, as was found to be effective in the case of the methionato-compound, owing to decomposition of the dimethylmalonic acid [Found: Co = 13·82; H_2O (at 130°) = 8·44. $C_9H_{22}O_4N_4BrCo,2H_2O$ requires Co = 13·87; H_2O = 8·47 per cent. Found: Br = 18·54. $C_9H_{22}O_4N_4BrCo$ requires Br = 18·80 per cent.].

The *nitrate*, $YNO_3,2H_2O$, was prepared by the interaction in solution of equivalent quantities of the bromide (1·134 grams) and silver nitrate (0·4532 gram). After shaking for one hour, the silver bromide was collected and the filtrate evaporated to low bulk on the water-bath. The salt crystallised out very slowly as a crimson, microcrystalline powder or in dark red crusts of indefinite shape * [Found: H_2O (at 130°) = 8·85.

$$C_9H_{22}O_7N_5Co,2H_2O$$

requires H_2O = 8·85 per cent. Found: Co = 15·58; N = 19·19. $C_9H_{22}O_7N_5Co$ requires Co = 15·89; N = 18·87 per cent.].

The *chloride*, $YCl,2H_2O$, was obtained by shaking a solution of the bromide with an excess of freshly precipitated silver chloride, collecting the precipitate, and evaporating the filtrate to low bulk. It separated in microcrystalline prisms, which are very soluble in water [Found: H_2O (at 130°) = 9·95.† $C_9H_{22}O_4N_4ClCo,2H_2O$ requires H_2O = 9·47 per cent. Found: Co = 16·86. $C_9H_{22}O_4N_4ClCo$ requires Co = 17·11 per cent.].

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* Both in the case of the nitrate and the chloride, which are very readily soluble in water, it was difficult to obtain a solution which was just of the right concentration for crystallisation; if too concentrated it formed a viscid mass.

† Only 0·2 gram of the salt was obtained, so that the estimation of the water of crystallisation could not be repeated. The high value found was probably due to the salt not being quite air-dry, owing to the abnormally damp weather which prevailed at the time: $3H_2O$ requires H_2O = 13·56 per cent.

CXX.—*The Constitution of Carbamides. Part XII. The Decomposition of Urea when Heated in Solution in the Presence of Acids.*

By Emil Alphonse Werner.

It was shown in Part V of the present series (T., 1918, **113**, 84) that the decomposition of urea, when heated in solution with hydrochloric acid, is primarily dependent on the dissociation of "free" urea present, thus:

Phase (1) $HN{:}C\begin{matrix}NH_2\\|\\O\end{matrix}$ $\longrightarrow$ (HNCO $\rightleftarrows$ HOCN) + NH_3.

The hydrolysis of cyanic acid, which follows immediately, proceeds at such a high velocity that both products of dissociation are removed practically as fast as they are generated. Urea fixed as a salt at the outset is thus rapidly "freed" to continue the first phase of the reaction.

Price (T., 1919, **115**, 1354) studied the decomposition of urea in the presence of nitric acid, and found that the reaction velocity at 100° was greater than with hydrochloric acid, as compared with the results obtained by Fawsitt (*Zeitsch. physikal. Chem.*, 1902, **41**, 601) with the latter acid. Because the addition of ammonium salts, and of certain salts containing an ion common with the ammonium salt, had a distinct accelerating effect on the decomposition of urea, Price inferred that the author's dissociation theory was apparently not applicable to the change in the presence of nitric acid.

Now, considering the straightforward character of the complete change, the second phase of which is as follows:

Phase (2) (HNCO $\rightleftarrows$ HOCN) + H_2O + $HX' = NH_4X' + CO_2$,

it is evident that the mechanism of the decomposition of urea must be similar with all acids.

The inference drawn by Price is the result of a misunderstanding, since striking proof in support of the dissociation theory has been supplied by his experiments, showing the effect of temperature on the velocity of the decomposition with nitric acid. Thus the values at 100°, 80°, and at 70° were represented by the respective ratios 102, 9·3, and 2·4. Such a great fall in velocity compared with a relatively small fall in temperature is explained by the fact that the dissociation of urea only starts at a fairly rapid rate at about 90°. At 60° it is almost nil (see remarks, Part V, *loc. cit.*, p. 94).

Again, as nitric acid is rather weaker than hydrochloric acid, the theory predicts that the velocity of the reaction should be greater in the presence of the former acid, since the concentration of "free" urea will be greater under similar conditions.

Proof that the amount of urea decomposed is greater* the weaker the acid is shown by a comparison of the following results obtained in the presence of acetic, nitric, and hydrochloric acids respectively.

The ratio of urea to acid was 1 : 2 molecular proportions.

The concentration at the outset was urea $= N/2$, acid $= N$.

The experiments were performed at 100° and under reflux for reasons which have been clearly pointed out before (Part V).

TABLE I.

Time.	Acetic acid. Per cent.	Nitric acid. Per cent.	Hydrochloric acid. Per cent.
1 hour	19·5	15·7	13·3
2 hours	31·8	25·8	23·2
3 „	(*a*) 41·0	35·0	32·2
4 „	(*b*) 53·4	46·4	40·8
5 „	(*c*) 64·2	57·0	48·4
	(Urea decomposed.)	(Urea decomposed.)	(Urea decomposed).

The above results were calculated from titrations of the residual acidity at the end of each experiment, with the exception of the values (*b*) and (*c*) for acetic acid, which were obtained from determinations of the residual urea, the only trustworthy method in these two cases. As the concentration of ammonium acetate produced during the reaction increased, there was loss of ammonia by its hydrolytic dissociation, whereby residual acidity gave too low a result. Whilst by the titration method (*b*) was approximately 47, and (*c*) 51, there was but little difference in the case of (*a*) when checked by the estimation of residual urea.

Whilst the velocity of phase (1) is directly proportional to the concentration of "free" urea, the amount of the latter in solution at any time is inversely proportional to the strength of the acid present, all other conditions being equal. Hence, after a certain time, a similar condition is attained, no matter what acid may be

* This is only demonstrable up to a certain point, for an interesting reason. When the concentration of a very weak acid, such as acetic, falls considerably as the reaction proceeds, it is unable to fix ammonia to complete the change of phase (2), with the result that more or less urea is regenerated, thus: $2HNCO + H_2O = CON_2H_4 + CO_2$. After potassium cyanate was added to an excess of a 2 per cent. solution of acetic acid, urea was detected in the solution.

present, since practically all the residual urea will be "free" when the concentration of acid has fallen very low as a result of its progressive neutralisation. For this reason, the decomposition of all the urea is a very tedious process (compare Fawsitt, *loc. cit.*)

Now, the decomposition of urea in the presence of acids is not an ionic change. "Free" urea is not ionised, and hence the contention that the addition of an ammonium salt, or of any salt, containing an ion common with the acid used should retard the velocity of decomposition does not hold.

The following results were obtained when ammonium nitrate ($N/4$ at outset) was added in the presence of acetic acid and of nitric acid respectively, and when ammonium chloride ($N/4$) was added in the presence of hydrochloric acid. The concentrations of urea and of acid were as before.

TABLE II.

Time.	Acetic acid + NH_4NO_3. Per cent.	Nitric acid + NH_4NO_3. Per cent.	Hydrochloric acid + NH_4Cl. Per cent.
1 hour	22·0	19·9	14·0
2 hours	35·1	31·78	29·1
3 „	45·4	37·40	41·2
	(Urea decomposed.)	(Urea decomposed.)	(Urea decomposed.)

As the reaction progressed, the concentration of ammonium salts increased, and in the case of the nitrate there was appreciable loss of ammonia during three hours' heating, and since the results show sufficiently the general acceleration when compared with the values in table I, experiments were not carried out beyond this period.

The acceleration of the decomposition of urea is here due to the hydrolytic dissociation of the ammonium salts, whereby the velocity of phase (1) is promoted. Whilst the constitution of the simple salts of ammonia is still unsolved, their dissociation* into acid and ammonia is a well-known fact, their ionisation is a phenomenon which has been assumed but never proved, and, in the author's opinion, it plays no part in the reactions under discussion.

The dissociation of "free" urea is much more sensitive to external conditions than might be supposed; thus, variations in the length and diameter of the reflux tube and in the shape and volume of the flask were sufficient to introduce distinct disturbing effects. Hence two flasks of similar form and volume, and the one reflux tube, were used in the experiments.

* The presence of moisture being necessary is evidence of its hydrolytic character.

The mode of decomposition of urea in the presence of acids (and of alkalis) is in itself sufficient to throw discredit on the "carbamide" formula.

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CXXI.—*Synthesis of Boranilides. Part I. Boranilide and its Derivatives.*

BY TARINI CHARAN CHAUDHURI.

THE chemical constitution and physiological action of anilides of organic acids have been studied in detail by Gibbs and Hare (*Amer. Chem. J.*, 1890, **11**, 435) and by Gibbs and Reichert (*ibid.*, 1891, **13**, 289).

It was hoped that, if boric acid could be combined with aniline to form boranilide, the latter would have important physiological properties, and it was with this object in view that the study of the condensation of aniline with boric acid was undertaken. From the stable boranilide which was obtained, a series of derivatives has been prepared.

Ditte (*Compt. rend.*, 1887, **105**, 813) prepared aniline borate, $NH_2Ph,2B_2O_3,4H_2O$, and Schiff (*Annalen, Suppl.*, 1867, **5**, 209) describes an "anilide of boric acid," prepared from ethyl borate and aniline, as being readily decomposed by water. It would appear that Schiff's compound was identical with that prepared by Ditte.

In the present work a mixture of molecular quantities of boric acid and aniline was heated at 135—140° with the addition of a small quantity of zinc chloride as condensing agent. Aniline does not, however, condense with orthoboric acid owing to the fact that at 100° orthoboric acid is converted into metaboric acid with the elimination of one molecule of water; so that condensation at the above temperature really takes place between aniline and metaboric acid.

As the condensation-products are very stable, it would appear that the nitrogen atom is directly linked with boron and not with oxygen; in the latter event the compounds would have been more easily hydrolysed than was found to be the case.

In the compounds described in this paper, the presence of the boric acid residue was detected in each case.

The well-known glycerol method for the quantitative estimation of boric acid (produced by decomposing the compounds with sulphuric acid with or without the addition of potassium dichromate) did not give satisfactory results. The estimation of carbon, although carefully carried out, was vitiated by the absorption of some volatile boric acid in the potash bulbs. The determination of the molecular weight of boranilide by analysis of the platinichloride as well as the estimation of nitrogen by Dumas' method conclusively show, however, that the condensation takes place between molecular quantities of boric acid and aniline, as stated above.

Boranilide satisfactorily responds to Tafel's colour reaction for anilides (*Ber.*, 1892, **25**, 412).

The constitution of boranilide, $C_6H_5{\cdot}NH{\cdot}BO$, is supported by the fact that it yields nitroso- and other derivatives exactly as would be expected. It appears, therefore, that the anilide, both in the free state and in acid solution, has the above constitution, whilst when dissolved in alkali hydroxide solution it has the tautomeric formula, $C_6H_5{\cdot}N{:}BOH$.

Experimental.

Boranilide, $C_6H_5{\cdot}NH{\cdot}BO$.

A mixture of 5 grams of boric acid and 7·5 grams of aniline was heated to 135—140°, when 1 gram of fused zinc chloride was added and the mixture stirred. The pasty mass became solid on cooling, and was successively extracted with small quantities of water. It was then washed with very dilute hydrochloric acid, and repeatedly washed with warm water. The substance crystallised from alcohol in white needles (6·5 grams), which did not melt at 212° (Found: N = 11·32; M.W. (from platinichloride) = 119·7. C_6H_6ONB requires N = 11·76 per cent. M.W. = 119·0).

Boranilide dissolves in acids or alkali hydroxides. The *hydrochloride* forms thin, green plates decomposing at 108—110° (Found: Cl = 22·40. C_6H_6ONB,HCl requires Cl = 22·82 per cent.). The *platinichloride* forms small, yellow crystals which gradually become green (Found: Pt = 30·28. $(C_6H_6ONB)_2H_2PtCl_6$ requires Pt = 30·09 per cent.).

Benzoylboranilide, $C_6H_5{\cdot}NBz{\cdot}BO$.

This was prepared by adding benzoyl chloride to a solution of boranilide in glacial acetic acid or by adding aqueous potassium

hydroxide to a solution of boranilide (6 grams) in benzoyl chloride (7 grams). The product is a white powder which melts at 166° (Found: C = 69·59; H = 4·87. $C_{13}H_{10}O_2NB$ requires C = 69·95; H = 4·48 per cent.).

Thioboranilide, $C_6H_5 \cdot NH \cdot BS$.

A mixture of boranilide and excess of flowers of sulphur was heated until the sulphur melted, when the anilide dissolved in it. The heating was continued for ten minutes. In another preparation boranilide was heated with phosphorus pentasulphide. In each case a hard solid was produced, which was powdered and repeatedly washed with warm carbon disulphide. A yellowish-grey powder was obtained, having a faint odour of mercaptan. It is insoluble in water, alcohol or ether, but soluble in acids, and melts at 109—110° (Found: N = 9·91. C_6H_6NSB requires N = 10·37 per cent.).

Nitrosoboranilide, $C_6H_5 \cdot N(NO) \cdot BO$.

Boranilide was dissolved in excess of hydrochloric acid and a solution of sodium nitrite added. A reddish-yellow oil was produced which solidified after some time to a brownish-pink solid. On adding alcohol to the oil it readily solidifies in plates melting at 83°. The substance dissolves in ether, and the ethereal solution responds to Liebermann's reaction (Found: N = 18·22. $C_6H_5O_2N_2B$ requires N = 18·91 per cent.).

Bromoboranilides, $C_6H_4Br \cdot NH \cdot BO$.

Of the three bromoboranilides which have been prepared, that having the highest melting point is assumed to be the para-, that with the lowest the ortho-, and the remaining one the meta-isomeride.

p-*Bromoboranilide*.

Bromine was added to an acetic acid solution of boranilide and the precipitate was shaken with chloroform; a white powder remained which consisted of an acetate soluble in water. On warming the aqueous solution with potassium carbonate solution, the free compound, melting at 121—122°, was obtained (Found: Br = 39·86. C_6H_5ONBrB requires Br = 40·44 per cent.).

o-Bromoboranilide.

On evaporating the chloroform solution obtained in the preceding experiment a pale pink powder was obtained, the aqueous solution of which, when warmed with potassium carbonate, gave a very pale yellow substance melting at 82° (Found: Br = 40·14. C_6H_5ONBrB requires Br = 40·44 per cent.).

m-*Bromoboranilide.*

This was prepared by the action of a sulphuric acid solution of bromine on a solution of boranilide in sulphuric acid. Almost black, minute crystals separated, the aqueous solution of which, when boiled with potassium carbonate, gave m-*bromoboranilide* as a violet powder melting at 96—97° (Found: Br = 40·10. C_6H_5ONBrB requires Br = 40·44 per cent.).

Conversion of meta- *into* ortho- *and* para-*Bromoboranilides.*

Without separating the almost black crystals from contact with sulphuric acid, and on boiling this *m*-bromo-derivative for a short time with water, a sudden change takes place and the black substance is converted into a pale pink powder. This is gently warmed with chloroform, when a white substance remains which dissolves in water. The aqueous solution, when boiled with potassium carbonate solution, yields a compound (m. p. 120—122°) which is evidently *p*-bromoboranilide, whilst the chloroform solution, on evaporation, gives a substance from which, when boiled with potassium carbonate, a pink powder (m. p. 83—84°) is produced, evidently the *o*-bromo-derivative.

Benzoyl-p-*bromoboranilide*, $C_6H_4Br{\cdot}NBz{\cdot}BO$.

Benzoyl chloride was gradually added to a solution of *p*-bromoboranilide in glacial acetic acid, when the solution became turbid. On shaking and allowing to remain, microscopic, white, cubic crystals separated, melting at 128—130° (Found: Br = 25·82. $C_{13}H_9O_2NBrB$ requires Br = 26·51 per cent.).

Boryldiazoaminobenzene, $C_6H_5{\cdot}N{:}N{\cdot}NPh{\cdot}BO$.

To 5 grams of nitrosoboranilide 3 grams of aniline were added, and then a mixture of hydrochloric acid, alcohol, and ether. On boiling, no action apparently took place, but on adding water and boiling the solution became red and a heavy oil separated, which,

on cooling and shaking, soon solidified to crystalline, red plates melting at 109°.

Above 130° the compound suddenly decomposes with a feeble explosion. During combustion by Dumas' method the burners below the mixture of the substance and copper oxide, as well as a little in front of and behind it, were kept very low. In spite of this precaution a low result for nitrogen was obtained owing to the rather sudden evolution, and consequently incomplete reduction, of the oxides of nitrogen (Found: N = 18·13. $C_{12}H_{10}ON_3B$ requires N = 19·29 per cent.).

Borylhydrazoaminobenzene, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}NPh{\cdot}BO$.

On adding stannous chloride and hydrochloric acid or zinc and hydrochloric acid to the red alcoholic solution of boryldiazoaminobenzene, the red solution soon became colourless, and the hydrazo-compound was isolated by rendering the solution alkaline and extracting with ether. It melts at 123—124°, dissolves in hydrochloric acid, and gives a yellow nitroso-derivative, which responds to Liebermann's reaction.

Boro-α-phenyl-β-aminophenylhydrazide, $NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}NPh{\cdot}BO$.

A solution of 4 grams of the above hydrazo-compound was boiled with concentrated hydrochloric acid, and the hydrochloride basified with ammonia. The greyish-yellow base (3·4 grams) is soluble in alcohol and melts at 163—166° (Found: N = 17·97. $C_{12}H_{12}ON_3B$ requires N = 18·66 per cent.).

Boro-α-phenylhydrazidobenzeneazophenol, $OH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}NPh{\cdot}BO$.

Four grams of the above base were diazotised and combined with 2 grams of phenol in alkaline solution. The brown product (5·4 grams) is sparingly soluble in cold water, more readily so in alcohol, and dissolves readily in acids or alkali hydroxides. It melts at 152—153° to a deep violet liquid.

The *hydrochloride* crystallises in dark brown needles.

The *dibenzoyl* derivative, $OBz{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NBz{\cdot}NPh{\cdot}BO$, prepared from 5 grams of the azo-compound by the Schotten-Baumann reaction (yield, 8·2 grams), is a pale brown substance insoluble in water, sparingly soluble in alcohol, but readily so in ether, from which it separates in needles melting at 113—115°.

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CXXII.—*The Ethylene-Oxide Structure of Sucrose and some Other Carbohydrates.*

By EDWARD FRANKLAND ARMSTRONG and THOMAS PERCY HILDITCH.

THE structural formula of sucrose has long been a subject of research; the more recent work of Haworth and Law (T., 1916, **109**, 1314) has afforded evidence that it is formed by the fusion of a molecule of α-glucose having the butylene-oxide structure and of α-fructose having the ethylene-oxide structure. When hydrolysed in presence of acids, these forms are the first to be produced, but subsequently they undergo, more or less rapidly, isomeric changes, forming, first, the corresponding butylene-oxide form of fructose and then the mixture of α- and β-modifications of this in equilibrium, and, secondly, the β-butylene-oxide form of glucose, as well as small quantities of the corresponding ethylene-oxide forms. The final mixture, which has the well-known optical rotatory power and other physical characteristics of invert-sugar, is thus a very complex mixture of substances, and there is little wonder that its crystallising power is low and that its nature is hard to establish.

Haworth and Law's proof of the presence of the ethylene-oxide form of fructose in sucrose is based on the complete methylation of the disaccharide and the identification of the methyl fructose formed after hydrolysis.

In a recent communication (T., 1919, **115**, 1410) we have adduced evidence of the existence in small proportions of an ethylene-oxide modification of glucose, fructose, etc., in presence of acid, and shown how the reduction of permanganate affords an indication of the amount of this form present. It appeared of interest, therefore, to use this method to detect the initial liberation of the ethylene-oxide form of fructose from sucrose, and so confirm the observations of Haworth and Law.

The quickest and most delicate method of hydrolysing sucrose is by means of invertase, and as the action is in neutral solution, the subsequent isomeric changes are relatively slow. The figures quoted in table I show a rapid increase in the reducing power to permanganate, and indicate conclusively the presence of what we consider to be the ethylene-oxide form of fructose, since the butylene-oxide form is relatively stable to permanganate.

When sucrose is hydrolysed in presence of hydrochloric acid, action is slower, and isomeric change is promoted by the acid. The figures in table II give very little indication of the presence of any more of the ethylene-oxide form than is normally produced by acid of this strength in a mixture of glucose and fructose, and presumably the ethylene-oxide form first produced had undergone rapid rearrangement into the butylene-oxide form in presence of the acid.

Anomalous results have been obtained, however, if the mixture of sugar and acid is neutralised before the addition of permanganate. These solutions appear to be approximately twice as sensitive to permanganate, and we are inclined to attribute this to some as yet unexplained disturbing factor other than the persistence of an excess of the ethylene-oxide form. It may be recalled that we observed that an acid solution of glucose or fructose, if neutralised simultaneously with the addition of permanganate, gave reduction times almost identical with those of the acid solution, and we considered that this indicated the persistence of the active form of the sugar after neutralisation of the acid had taken place.

In our previous communication we drew attention to the relative activities of glucose, mannose, and fructose towards permanganate, both in acid and in alkaline solution. We have now made similar experiments with galactose, arabinose, and xylose. The comparative times of reduction of the standard quantity of permanganate by acid and alkaline solutions of these sugars, and by the respective solutions when neutralised simultaneously with the addition of permanganate, are:

Age of Solution :—	*N*/10-HCl.				*N*/18-NaOH.			
	Fresh.		Five hours.		Fresh.		Five hours.	
	Acid.	Neutd.	Acid.	Neutd.	Alk.	Neutd.	Alk.	Neutd.
Glucose	29·0	27	29·0	28	11	180	3·0	48
Mannose	13·0	12	12·0	12	25	90	9·0	46
Fructose	17·0	15	16·0	18	3	60	1·25	11
Galactose	8·0	12	5·5	21	26	26	3·5	Indef.
Arabinose	2·5	11	2·5	11	31	38	1·5	75
Xylose	4·0	20	6·0	18	18	32	1·5	75

With the single exception of mannose, there is relatively little difference between the sugars in their behaviour in alkaline solution, and it would appear that the configuration of the rest of the molecule has but little effect on the readiness to undergo enolisation.

In acid solution the differences are more marked, the pentoses being especially active as reducing agents: there is no very apparent connexion between activity and configuration.

The proof of the existence of ethylene-oxide forms of the simple sugars has introduced a new conception into the structural chemistry of the carbohydrates which may have far-reaching significance. In consequence, until further experimental evidence has been accumulated, it is advisable to exercise caution in the interpretation of differences between the various sugars such as we have just recorded. As it may be some time before we can return to this investigation, we wish to place the facts on record for the benefit of other workers in this field.

Experimental.

Hydrolysis of Sucrose by Invertase.

A quantity of pressed yeast was autolysed in the presence of toluene for some days, and the aqueous filtrates were precipitated by excess of alcohol; the invertase was collected, redissolved in a little water, and again precipitated by alcohol. The filtered product was dissolved in water and the solution divided into three equal portions: two of these were employed in the hydrolysis of 250 c.c. of $M/36$- and $5M/36$-solutions of sucrose (giving total hexose concentrations of $M/18$ and $5M/18$, as in our former work), whilst the third was made up to 250 c.c. with pure water.

The solutions were maintained at 25°, and 10 c.c. portions were tested from time to time with 2 c.c. of $N/100$-permanganate; the colour changes were not the same as with acid solutions, but two fairly definite tints were observable, namely, a clear brown immediately after the last trace of pink had faded, and, finally, a very clear pale yellow.

The solution of invertase in water alone was tested with the others, and it was found that reduction of the permanganate was very slow, the clear brown only being reached after seventy to ninety minutes, whilst the further change to pale yellow occupied many hours.

An attempt was made to examine the effect of introducing

N/10-hydrochloric acid on the permanganate test, but it appeared that in presence of acid the invertase alone acquired the power of very rapidly reducing permanganate.

Table I illustrates the results obtained with invertase in neutral solutions of M/36- and $5M$/36-sucrose, with the corresponding optical rotatory power of the solutions.

TABLE I.

	M/36-Solution.			$5M$/36-Solution.		
	Permanganate test.			Permanganate test.		
Age of solution (hours).	Brown. (minutes.)	Yellow. (minutes.)	$[\alpha_D]$.	Brown. (minutes.)	Yellow. (minutes.)	$[\alpha_D]$.
0·0	45	100	+61·5°	30	100	+63·3°
0·5	35	53	41·7	15	28	54·7
1·0	25	35	28·3	10	22	45·7
1·5	22	35	20·0	8	18	38·3
2·5	20	30	—	8	19	—
3·0	19	25	—	8	15	—
3·5	19	26	1·7	7	14	12·3
4·5	20	25	10·0	7	11	2·7
5·5	20	25	18·3	6	9	− 6·0
10·3	20	25	20·0	6	9	18·0
24·0	20	25	21·5	6	9	21·0

Hydrolysis of Sucrose by N/10-*Hydrochloric Acid.*

TABLE II.

	M/36-Solution.		$5M$/36-Solution.		
	Permanganate test.		Permanganate test.		
Age of solution (hours).	Acid. (minutes.)	Neutd. (minutes.)	Acid. (minutes.)	Neutd. (minutes.)	$[\alpha_D]$.
0·0	230*	110*	142	57	+62·8°
1·0	155	40*	120	30	59·0
3·0	115	36*	60	27	—
5·0	100	16†	49	23	49·0
23·7	35	27	19	17	32·3
30·0	—	—	16	10	24·0
72·3	31	17	18	10	4·0

* Indefinite end-point. † Precipitation set in.

Mean Comparative Figures for Fructose and Glucose.

The following are the mean times of reduction of permanganate, in the acid and neutralised tests, found in the former work for solutions of fructose and glucose in N/10-hydrochloric acid:

	M/18-Fructose (found).	*M*/18-Glucose (found).	Calculated mean of *M*/18-fructose and *M*/18-glucose.	*M*/36-Fructose+ *M*/36-Glucose (found).
Acid	16·5	29·2	22·9	22·8
Neutralised	17·0	28·0	22·3	26·8

	5*M*/18-Fructose (found).	5*M*/18-Glucose (found).	Calculated mean of 5*M*/18-fructose and 5*M*/18-glucose.
Acid	7·7	19·4	13·6
Neutralised ...	7·8	19·0	13·4

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CXXIII.—*Triethylene Tri- and Tetra-sulphides.*

By Sir PRAFULLA CHANDRA RÂY.

IN the preparation of ethylene mercaptan by the interaction of ethylene dibromide and alcoholic potassium hydrogen sulphide, after removal of alcohol and ethylene mercaptan by steam distillation, continued passage of steam furnishes a milky distillate solidifying to a crystalline mass, which, when recrystallised from hot alcohol, melts at 113°, and consists of *triethylene trisulphide*, $(C_2H_4)_3S_3$. The non-volatile oil remaining in the distilling flask also solidified on cooling to a crystalline mass, consisting of a mixture of three polymeric *triethylene tetrasulphides*. By extraction with alcohol, the α-modification (m. p. 76°) was obtained; the remainder, on extraction with benzene, gave the β-modification (m. p. 102—104°), and the insoluble residue furnished the γ-modification (m. p. 116°). The alkaline liquid which remained behind in the flask yielded, on acidification, an oil, which has been proved to be *triethylene disulphide dimercaptan*, $(C_2H_4)_3S_2(SH)_2$. On treatment with mercuric chloride, it gave the corresponding *chloromercaptide*, $(C_2H_4)_3S_2(SHgCl)_2$. This dimercaptan, when treated in ethereal solution with an alcoholic solution of iodine, gives the β-tetrasulphide (m. p. 104°), and its methyl-alcoholic solution slowly oxidises in the air to *δ-triethylene tetrasulphide* (m. p. 59—60°). The molecular weight of this variety was found to be 816, which corresponds with four times the formula, $(C_2H_4)_3S_4$. The β-modification is sparingly soluble in boiling benzene or chloroform, and its molecular weight could not be

determined with exactness, but evidence pointed to its having a much higher molecular weight, indicating that in this case there was a coalescence of more than four simple molecules. In boiling chloroform, the substance undergoes partial slow spontaneous polymerisation, as was proved by the fact that successive crops differed in melting point and were only sparingly soluble in benzene. The insoluble portion melted at about 114°.

It seems probable that the γ-modification, which is insoluble in ordinary solvents, has a much higher molecular weight.

The formation of the compounds may be explained according to the following scheme. The alcoholic solution of potassium hydroxide, on being saturated with hydrogen sulphide, contains potassium sulphide in addition to potassium hydrogen sulphide, and this mixture acts on ethylene dibromide, thus:

$$3C_2H_4Br_2 + K_2S + 2KSH \longrightarrow SH\cdot C_2H_4\cdot S\cdot C_2H_4\cdot S\cdot C_2H_4\cdot SH.$$

Evidently, the tetrasulphides are the products of spontaneous aerial oxidation of the dimercaptan, thus:

$$\underline{S\cdot C_2H_4\cdot S\cdot C_2H_4\cdot S\cdot C_2H_4\cdot S}$$

The formation of the trisulphide may be explained thus:

$$3C_2H_4Br_2 + 3K_2S = C_2H_4\begin{<}{S\cdot C_2H_4 \atop S\cdot C_2H_4}\end{>}S + 6KBr.$$

Experimental.

The method of preparation (from 100 grams of ethylene dibromide) was exactly as described by Fasbender (*Ber.*, 1887, **20**, 461). After removal of alcohol and ethylene mercaptan by means of steam, there separated from the distillate a solid, which was pressed on porous plate (1·29 grams) and crystallised from alcohol, when it melted at 113°, and consisted of *triethylene trisulphide* (Found*: C = 37·84; H = 6·80; S = 53·06, 53·54. $C_6H_{12}S_3$ requires C = 40·00; H = 6·67; S = 53·33 per cent.).

The non-volatile oil, which solidified on cooling (6·5 grams), was

* As these compounds are very rich in sulphur, the length of the lead chromate in the combustion tube was much increased so as to preclude the possibility of sulphur dioxide escaping absorption. Moreover, in some cases the alkali hydroxide in the potash bulb, after analysis, was oxidised with bromine, warmed and acidified with hydrochloric acid and treated with barium chloride, but no barium sulphate could be detected.

In the estimation of sulphur, Carius' method was adopted by which the compound was converted into the sulphonic acid. The acids were neutralised with sodium carbonate, evaporated to dryness, and then fused with potassium nitrate so as to transform the sulphonate into sulphate.

extracted completely with hot alcohol, the solution furnishing crystals of *α-triethylene tetrasulphide* melting at 75° (Found: C = 33·88; H = 7·42. $C_6H_{12}S_4$ requires C = 33·96; H = 5·66 per cent.).

The residue was then similarly treated with boiling benzene, which extracted *β-triethylene tetrasulphide* melting at 102—104° (Found: C = 33·92; H = 6·94. $C_6H_{12}S_4$ requires C = 33·96; H = 5·66 per cent.).

The final insoluble portion consisted of *γ-triethylene tetrasulphide* melting at 116° (Found: C = 34·30, 33·59; H = 6·41, 7·90; S = 59·07. $C_6H_{12}S_4$ requires C = 33·96; H = 5·66; S = 60·38 per cent.).

The alkaline liquid, on acidification, gave an oil, which was extracted with ether (8·5 grams), and consisted of *triethylene disulphide dimercaptan* boiling at 260—263° (Found: S = 60·86. $C_6H_{14}S_4$ requires S = 59·80 per cent.).

Its methyl-alcoholic solution, on exposure to air, gave *δ-triethylene tetrasulphide* melting at 59—60° (Found: C = 33·05; H = 6·29; S = 60·55. M.W. by ebullioscopic method in chloroform = 815·5, 815·8. $C_{24}H_{48}S_{16}$ requires C = 33·96; H = 5·66; S = 60·38 per cent. M.W. = 848).

On treatment with mercuric chloride, it gave the *dichloromercaptide* (Found: C = 10·34; H = 2·22; Cl = 9·40, 10·81; S = 18·54; Hg = 58·44. $C_6H_{12}Cl_2S_4Hg_2$ requires C = 10·54; H = 1·75; Cl = 10·40; S = 18·74; Hg = 58·57 per cent.).

Various derivatives of the above polysulphides are in course of preparation.

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CXXIV.—*The Oxidising Properties of Sulphur Dioxide. Part I. Iron Chlorides.*

By WILLIAM WARDLAW and FRANCIS HERBERT CLEWS.

As this paper has to deal with the reactions of sulphur dioxide and metallic chlorides, it may be well to summarise our present knowledge relative to this subject. The oxidation of stannous chloride by sulphur dioxide in the presence of concentrated hydrochloric acid has been shown (Smythe and Wardlaw, *Proc. Durham Phil. Soc.*, 1914, **5**, 187) to proceed quantitatively to completion according to the equation

$$3SnCl_2 + SO_2 + 6HCl = 3SnCl_4 + 2H_2O + H_2S.$$

Sulphurous acid is reduced by titanous chloride to hyposulphurous acid (Knecht, *Ber.*, 1903, **36**, 166), and its further reduction to sulphur was noticed by the same investigator. Smythe and Wardlaw (*loc. cit.*) further proved that when sulphur dioxide is passed into a warm, strongly acid solution of titanous chloride hydrogen sulphide is freely evolved. Sulphur is formed by secondary reaction between the hydrogen sulphide and the sulphur dioxide, and if the escaping hydrogen sulphide is led into an excess of sulphur dioxide in concentrated hydrochloric acid, the reaction which goes to completion may be quantitatively summarised as follows:

$$3SO_2 + 12TiCl_3 + 12HCl = 12TiCl_4 + 6H_2O + 3S.$$

The same authors (*loc. cit.*) have shown that sulphur dioxide oxidises mercurous chloride in the presence of concentrated hydrochloric acid according to the equation

$$SO_2 + 4HCl + 2Hg_2Cl_2 = 4HgCl_2 + 2H_2O + S.$$

In the same paper it was mentioned that in concentrated hydrochloric acid, ferrous chloride is oxidised by sulphur dioxide to ferric chloride, with the formation of sulphur. No sulphuric acid was detected in the solution. This reaction differed from those already quoted in that oxidation under the most favourable conditions proceeded only to a limited extent, the average yield of ferric iron in all the experiments being 7 per cent. of the total iron present, the extremes being 4 and 11·6 per cent. In these experiments, rigid control was not exercised over the conditions of temperature, concentration, etc., and it seemed desirable, therefore, that a systematic investigation of this reaction should be carried out.

Experimental.

The general method of procedure was as follows. Pure electrolytic iron was dissolved in pure concentrated hydrochloric acid contained in a flask made entirely of glass, and such that the reacting gases could be passed through the solution contained in it. This was connected with wash-bottles containing water and sodium hydroxide solution respectively. These served to absorb the effluent sulphur dioxide and hydrogen chloride and to exclude air, and so prevent atmospheric oxidation. The temperature of the flask was controlled by immersion in an oil-bath. A stream of carbon dioxide was continuously passed through the apparatus during the solution of the metal. When the iron had completely dissolved, the flask was connected with a sulphur-dioxide syphon and the gas passed for a stated period. It was noticed that after the sulphur dioxide had passed for a few minutes the solution changed to olive-green, then to reddish-brown, and became distinctly opalescent, owing to the separation of sulphur. After the reaction had proceeded for the required time, the sulphur dioxide was displaced by carbon dioxide, the solution cooled in a stream of the same gas, and the iron titrated, after suitable dilution with air-free water, with standard potassium dichromate according to Zimmermann and Reinhardt's method. The sulphur was determined by filtration and direct weighing.

Quantitative Aspect of the Reaction.

There are two possible reactions involved, corresponding (*a*) with direct reduction of the sulphur dioxide to sulphur, and (*b*) with initial reduction of the sulphur dioxide to hydrogen sulphide, which reacts with excess of sulphur dioxide, forming sulphur. Both reactions are represented, finally, by the equation

$$SO_2 + 4HCl + 4FeCl_2 = 4FeCl_3 + 2H_2O + S,$$

so that it is impossible to decide quantitatively between the two. Moreover, owing to the fact that the limit of reaction has been shown to be so soon reached, the accurate estimation of the small quantity of sulphur is very difficult.

The following are examples of the results obtained by Smythe and Wardlaw (*loc. cit.*).

Table I.

Experiment.	Concentration of ferrous solution.	Ferric iron produced. Gram.	Sulphur. Found. Gram.	Sulphur. Calc. Gram.
1	5·893 grams Fe per 100 c.c.	0·683	0·062	0·098
2	4·458 „ „ 200 c.c.	0·392	0·040	0·056
3	5·450 „ „ 200 c.c.	0·340	0·035	0·048

The conclusion to be drawn is that the equation mentioned above represents the reaction. From general considerations, one is also led to infer that it undoubtedly follows the course (*a*). Although hydrogen sulphide has never been directly detected in the reaction, from the fact that sulphur is formed in the neck of the flask and in the outlet tubes, it is possible that the reaction follows the course (*b*) to a very limited extent.

Influence of Concentration of Total Iron.

A range of concentrations of iron was investigated by dissolving varying quantities of iron (1—10 grams) in 250 c.c. of concentrated hydrochloric acid. Sulphur dioxide was passed through the solution for four hours at 115°, and the amount of ferric salt subsequently determined by titration.

TABLE II.

Experiment.	4.	5.	6.	7.	8.
Grams of iron dissolved in 250 c.c. of acid	1	3	5	7	10
Ferric iron per cent.	5·3	4·2	3·4	3·3	3·6

These results tend to show that the limit of oxidation is not influenced by the initial concentration of the iron. The concentration of the hydrochloric acid is not exactly constant in these experiments, owing to the varying losses of hydrogen chloride during the solution of the different quantities of metal, and this undoubtedly influences the degree of oxidation.

TABLE III.

Influence of Temperature.

Concentration.—Two grams of iron in 100 c.c. of concentrated hydrochloric acid.

Duration of Experiments.—Two and a-half hours.

Experiment	9.	10.	11.	12.	13.	14.	15.
Temperature	61°	70	79	93	115	125	gently boiling.
Ferric iron per cent....	1·6	3·0	3·5	5·2	3·8	3·0	2·8

The existence of an optimum temperature (approximately 95°) is the result of two or more opposing factors. The reaction-velocity will be favoured by an increase in temperature, whilst the higher temperature will lead to a more rapid loss of hydrochloric acid,

especially in the early stages of the reaction. It is also highly probable that the solubility of the sulphur dioxide decreases with rise in temperature.

Influence of the Concentration of Hydrochloric Acid.

The three following experiments are modifications of those described in table III with a view to change the concentration of hydrochloric acid. Values from table III are added for comparison.

TABLE IV.

Concentration.—Two grams of iron dissolved in 100 c.c. of concentrated hydrochloric acid.

Duration of Experiment.—Two and a-half hours.

Experiment.	Description.	Temperature.	Ferric iron / Total iron × 100.	From Table III. Ferric iron. Per cent.
16	Sulphur dioxide passed through concentrated hydrochloric acid at 95° before being led into the ferrous chloride solution	95°	7·8	5·2
17	Mixture of hydrogen chloride and sulphur dioxide (60 per cent. of HCl by weight)* passed into ferrous chloride solution	115	4·7	3·8
18	Carbon dioxide passed through ferrous chloride solution at 115° for 30 minutes and then sulphur dioxide for 2½ hours	115	1·3	3·8

* In all cases the composition of gaseous mixtures of sulphur dioxide and hydrogen chloride will be expressed by the percentage of each constituent by weight.

The increased yields in experiments 16 and 17, and diminished yield in experiment 18, in which excess of hydrochloric acid is removed from the solution, show that the oxidising effect of sulphur dioxide is only appreciable at concentrations exceeding that of the mixture of constant boiling point.

Accordingly, in the next experiments (table V) iron was dissolved in hydrochloric acid diluted to the concentration of the mixture of constant boiling point, and a mixture of hydrogen chloride and sulphur dioxide in different proportions passed into the ferrous chloride solution.

The ratio of sulphur dioxide to hydrogen chloride was observed by diverting a small proportion of the gases, by means of a T-piece, while the experiment was in progress. The acid gases were absorbed in 50 c.c. of *N*-sodium hydroxide, the chloride being sub-

sequently titrated with standard silver nitrate and ammonium thiocyanate, and the sulphite with standard iodine and sodium thiosulphate.

TABLE V.

Concentration.—Two grams of iron dissolved in 100 c.c. of hydrochloric acid (22 per cent. HCl).
Duration of Experiment.—Four hours.
Temperature.—115°.

Experiment.	Percentage composition of mixed gases. SO_2.	HCl.	$\frac{\text{Ferric iron}}{\text{Total iron}} \times 100$.
19	81·7	18·3	2·3
20	56·7	43·3	2·2
21	22·5	77·5	4·2
22	15·8	84·2	8·6
23	10·1	89·9	3·9

The results show that for the conditions described in the above experiments there is a comparatively narrow range of composition between 10 and 20 per cent. of sulphur dioxide which is most favourable for the oxidation of ferrous chloride, a maximum being reached in the neighbourhood of 16 per cent. of sulphur dioxide.

Limiting Concentration of Hydrochloric Acid for Oxidation of Ferrous Chloride by Sulphur Dioxide.

Since in dilute hydrochloric acid solution sulphur dioxide completely reduces ferric chloride to ferrous chloride, there will be

TABLE VI.

Temperature.—95°.
Duration of Experiment.—Four hours.
Solution.—Five grams of iron dissolved in acid specified in columns 2 and 3.

Experiment.	Concentrated hydrochloric acid. c.c.		Water. c.c.	Free HCl in 1000 c.c. of solution. Gram.	Remarks.
40	160	+	90	210·5	Little oxidation; about 0·5 per cent.
41	140	+	110	179·3	Very little oxidation; not measured.
42	130	+	120	165·8	Minute oxidation as shown by sulphur deposit.
43	125	+	125	165·1	No oxidation as shown by sulphur deposit.

some concentration of acid below which it is impossible to observe the oxidation of ferrous chloride by sulphur dioxide.

Iron was dissolved in acids of different concentrations, and the action of sulphur dioxide for four hours at 95° was observed.

For the analysis, a portion of the solution was withdrawn, weighed, and, after removal of the sulphur dioxide, diluted to a convenient volume. The iron and total chloride were determined, and from the difference the "free" hydrochloric acid was calculated. The specific gravity of the remainder of the solution was determined in order to state the concentration in grams per litre (see table VI).

It is concluded that oxidation by sulphur dioxide does not occur in ferrous chloride solutions containing less than 165 grams per litre of "free" hydrogen chloride.

Limit of Oxidation of Ferrous Chloride by Sulphur Dioxide in Hydrochloric Acid Solution.

(a) *Experiments at Atmospheric Pressure.*—With the purpose of determining the limit of oxidation, use was made of a rather larger flask fitted with a water-cooled exit tube, and containing an amount of solution sufficient to provide two samples for analysis.

Five grams of iron dissolved in 250 c.c. of concentrated hydrochloric acid (33 per cent.) were treated with hydrogen chloride and sulphur dioxide at 115°, as described in the following experiments.

TABLE VII.

Experiment.	Description.	Time of taking sample from commencement of experiment.	$\frac{\text{Ferric iron}}{\text{Total iron}} \times 100$.
24	Hydrogen chloride and sulphur dioxide (80 and 20 per cent.) passed continuously into ferrous chloride solution.	4 hours	2·2
		8 „	3·0
25	Hydrogen chloride and sulphur dioxide (50 per cent.) passed into ferrous chloride solution.	4 „	4·3
		6½ „	4·1
26	Sulphur dioxide alone passed for half an hour, then hydrogen chloride and sulphur dioxide (50 per cent.) continuously.	4 „	4·8
		8 „	4·7
27	Sulphur dioxide alone passed for half an hour, then hydrogen chloride and sulphur dioxide (80 and 20 per cent.)	3 „	3·5
		6½ „	7·1

TABLE VII (*continued*).

Experiment.	Description.	Time of taking sample from commencement of experiment.	Ferric iron / Total iron × 100.
28	*The ferrous chloride solution was alternately cooled to 30° (1 hour) and then quickly raised to 115° (heated for 2 hours), hydrogen chloride and sulphur dioxide (50 per cent. of each) passed continuously).	3 hours	6·5
		6 „	7·0
29	Experiment 28 repeated but cooled for 1 hour and heated to 115° for 1 hour.	6 „	8·8

* This procedure enabled the solution to absorb a large amount of the gases at the lower temperatures. On rapidly raising the temperature to 115° the solubility values would not be attained immediately, and during this interval the temporarily increased concentration of hydrochloric acid and sulphur dioxide would be available for reaction with the ferrous salt.

An oxidation of 8·8 per cent. (in experiment 29) is the highest obtained by the action of sulphur dioxide on ferrous chloride operating under a pressure slightly in excess of the atmospheric.

(b) *Experiments with Sealed Tubes.*—A rather higher degree of oxidation was obtained by the use of a sealed tube.

Expt. 30.—Half a gram of iron was dissolved in 10 c.c. of concentrated hydrochloric acid in a Carius tube in a current of carbon dioxide. The tube was immersed in ice, the solution saturated with sulphur dioxide, and the tube sealed. It was then heated at 100° for six hours and allowed to cool overnight. Titration showed that oxidation had occurred to the extent of 9·5 per cent., a value only slightly in excess of those obtained under normal pressures.

Limit of Reduction of Ferric Chloride by Sulphur Dioxide in Concentrated Hydrochloric Acid Solution.

(a) *Experiments under Atmospheric Pressure.*—It is well known that excess of hydrochloric acid prevents the complete reduction of ferric chloride by sulphur dioxide (Treadwell and Hall, "Quantitative Analysis," 5th ed., p. 607, footnote). It was not known, however, to what concentration of hydrochloric acid this referred or the extent to which ferric chloride was reduced.

Since the reduction of ferric chloride in concentrated hydrochloric acid was found to proceed slowly, mixtures of ferrous and ferric chlorides were prepared and their compositions determined,

both before and after passing sulphur dioxide and hydrogen chloride (approximately 50 per cent. of each gas) for a definite time. By this means, the value to which the reduction would eventually attain was estimated.

TABLE VIII.

Concentration.—Five grams of iron in 250 c.c. of hydrochloric acid (33 per cent.).

Temperature.—115°.

Gas.—SO_2 + HCl (50 per cent. mixture).

Experiment.	Duration of experiment. Hours.	$\frac{\text{Ferric iron}}{\text{Total iron}} \times 100$. Initial value.	Final value.	Reduction gradient (average reduction per hour).	Remarks.
31	4·0	100·0	78·2	5·4	Sulphate formed.
32	4·0	72·2	68·3	0·98	"
33	6·3	53·8	48·5	0·84	"
34	4·0	42·1	39·3	0·70	"
35	6·0	20·7	18·3	0·40	"
36	2·5	18·3	18·3	—	—
37	5·6	10·8	10·7	—	No sulphate.

No sulphur was formed in any of the above experiments. Apparently iron solutions containing more than 18·3 per cent. of ferric iron are slowly reduced by sulphur dioxide in the presence of concentrated hydrochloric acid. There seems also to be a range of from 10 to 18·3 per cent. of ferric iron in which there is no evidence of reduction or oxidation by the sulphur dioxide during the time of the experiments. Evidently this represents a zone in which the rate of reaction of the sulphur dioxide is very slow.

The solution in experiment 37 was analysed, and it was shown to contain in 1 litre 239 grams of "free" hydrochloric acid and 0·314 gram of sulphur dioxide.

(b) *Experiments in Sealed Tubes.*—Five grams of ferric chloride were dissolved in 10 c.c. of hydrochloric acid (33 per cent.), and the solution was saturated with sulphur dioxide at 0°. The tube was sealed and heated to 110° for four hours. Analysis showed a reduction of 20·6 per cent., and sulphuric acid was detected in the solution. A similar experiment after twenty-five hours at 110° gave only 22·3 per cent. of reduction. Apparently the high concentration of hydrochloric acid which exists in a closed vessel inhibits the reduction by sulphur dioxide, just as a high concentration of acid appears also to favour the oxidation of ferrous chloride.

Reduction of Ferric Chloride by Sulphur.

Stokes (*Bull. U.S. Geol. Survey*, No. 186, 1901) has examined the action of pyrites and marcasite on a hot dilute solution of ferric chloride, and observed reduction to a considerable extent (65 per cent. of the sulphur), the sulphur being oxidised to sulphuric acid. The present authors find that the action of sulphur in concentrated hydrochloric acid on ferric chloride is slight.

A solution of 5 grams of ferric chloride in 50 c.c. of concentrated hydrochloric acid was boiled in an atmosphere of carbon dioxide for one and a-half hours. The reduction corresponded with 0·65 per cent., the sulphur being oxidised to sulphuric acid. A solution of 3 grams of ferric chloride in 50 c.c. of concentrated hydrochloric acid to which 50 c.c. of colloidal sulphur solution were added, on boiling for one and a-half hours resulted in 1·7 per cent. of reduction. Sulphuric acid was produced. Experiments on the lines of those shown in table VIII, in which a proportion of finely divided sulphur was added, showed that it exerted very little reducing action in comparison with the sulphur dioxide.

Summary.

(1) The oxidation of ferrous chloride by sulphur dioxide can be represented quantitatively by the equation

$$4FeCl_2 + SO_2 + 4HCl = 4FeCl_3 + 2H_2O + S.$$

(2) The degree of oxidation is independent of the initial concentration of total iron.

(3) The most favourable temperature for the oxidation by sulphur dioxide of a solution of ferrous chloride in 33 per cent. hydrochloric acid is 95°.

(4) Oxidation by sulphur dioxide at 95° does not occur in solutions of ferrous chloride containing less than 165 grams per litre of "free" hydrogen chloride.

(5) A solution of ferrous chloride in hydrochloric acid of constant boiling point (22 per cent.) at 115° gave a maximum oxidation of 8·6 per cent. (ferric iron) when treated with a mixture of sulphur dioxide and hydrogen chloride containing 16 per cent. of sulphur dioxide.

Mixtures containing 10 to 20 per cent. of sulphur dioxide are most favourable for oxidation under the above conditions.

(6) The highest percentage of ferric iron obtained in any of the flask experiments recorded in this paper was 8·8. This result was produced by treatment of a ferrous chloride solution in 33 per cent.

hydrochloric acid at 115° with a 50 per cent. mixture of sulphur dioxide and hydrogen chloride under special conditions.

(7) Sealed-tube experiments gave a maximum oxidation of 9·5 per cent. of ferric iron.

(8) Iron solutions containing 10 to 18·3 per cent. of ferric iron in 33 per cent. hydrochloric acid at 115° showed no evidence of oxidation or reduction when a 50 per cent. mixture of sulphur dioxide and hydrogen chloride was passed into them for varying periods.

(9) Under the same experimental conditions as in (8), iron solutions containing more than 18·3 per cent. of ferric iron were slowly reduced.

(10) Ferric chloride in concentrated hydrochloric acid was reduced to a small extent by sulphur.

Theoretical.

The oxidation of a ferrous chloride solution by sulphur dioxide has been shown to be quantitatively represented by the equation

$$4FeCl_2 + SO_2 + 4HCl = 4FeCl_3 + 2H_2O + S \quad . \quad . \quad . \quad (1)$$

Moreover, since sulphur is able to reduce ferric chloride to some extent, it seems justifiable to assume that the above equation is reversible.

$$4FeCl_2 + SO_2 + 4HCl \rightleftharpoons 4FeCl_3 + S + 2H_2O \quad . \quad . \quad . \quad (2)$$

This fact is generally obscured, however, by the more general equation

$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + 2HCl + H_2SO_4 \quad . \quad . \quad . \quad (3)$$

Since no sulphuric acid is detected when a pure ferrous chloride solution is oxidised by sulphur dioxide in the presence of concentrated hydrochloric acid, it can be assumed that under these conditions the reaction that occurs is solely represented by equation (2). Moreover, seeing that sulphuric acid is only detected when sulphur dioxide in the presence of concentrated hydrochloric acid reacts with iron solutions containing more than 18·3 per cent. of ferric iron, it appears that reaction (3) is only operative in such solutions.

The idea that a reversible reaction takes place when pure ferrous chloride solution is oxidised by sulphur dioxide receives added support from the fact that only a limited yield of ferric salt is possible, and that the reaction is not greatly influenced by the initial concentration of total iron. Applying the law of mass action to equation (2), it appears that for a given concentration of sulphur dioxide and hydrogen chloride the equilibrium position would be

determined solely by the ratio of ferrous to ferric iron, assuming that the active masses of the sulphur and water are constant. The importance of a high concentration of hydrogen chloride to bring about the oxidation also follows logically from the idea of a balanced reaction.

The dependence of sulphur dioxide as an oxidising agent on a high concentration of hydrochloric acid has led to the suggestion that hydrochloric acid and sulphur dioxide interact, forming thionyl chloride to a small extent (Smythe and Wardlaw, *loc. cit.*). This idea receives support from the following reactions with the mercaptans:

$$SOCl_2 + 4R{\cdot}SH = R_2S_2 + R_2S_3 + H_2O + 2HCl$$

(Holmberg, *Annalen*, 1908, **359**, 81),

$$SO_2[+HCl] + 4R{\cdot}SH = R_2S_2 + R_2S_3 + 2H_2O[+HCl]$$

(Smythe and Forster, T., 1910, **97**, 1195).

On this assumption, the reaction

$$SOCl_2 + H_2O \rightleftharpoons SO_2 + 2HCl$$

must be reversible. Although this has not been proved directly, there is some indirect evidence in that when thionyl chloride reacts with mercaptans at low temperatures (0° to −70°), hydrogen chloride and sulphur dioxide are evolved, and water is found among the residual products (Tasker and Jones, T., 1909, **96**, 1904, 1910). In addition, the reactions of the sulphoxides and the haloid acids are to some extent analogous.

$$CH_3{\cdot}SO{\cdot}C_6H_4{\cdot}CH_3 + 2HBr \rightleftharpoons CH_3{\cdot}SBr_2{\cdot}C_6H_4{\cdot}CH_3 + H_2O$$

(Zincke and Frohneberg, *Ber.*, 1910, **43**, 837),

$$(CH_2Ph)_2SO + 2HBr \rightleftharpoons (CH_2Ph)_2SBr_2 + H_2O$$

(Fromm and Raiziss, *Annalen*, 1910, **374**, 90; Fromm, *ibid.*, 1913, **396**, 75).

From this idea, the question arises as to whether the oxidising properties of sulphur dioxide are only operative in the presence of concentrated hydrochloric acid. Experiments have been in progress to determine this point, and the results will be communicated in a further paper.

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CXXV.—*The Hydrolysis of Platinum Salts. Part I. Potassium Platinichloride.*

By Eben Henry Archibald.

While carrying out a series of experiments on the solubility of potassium platinichloride (Archibald, Wilcox, and Buckley, *J. Amer. Chem. Soc.*, 1908, **30**, 747), it was noticed that this salt undergoes hydrolysis in aqueous solutions at the ordinary temperature. Some time later, while studying the conductivity of some platinum compounds (Archibald and Patrick, *ibid.*, 1912, **34**, 369), it was found that this hydrolytic decomposition proceeded much more rapidly when the solutions were exposed to the action of light. As the extent to which this reaction has taken place in any given time could be measured very accurately, whilst the rate at which it proceeded was sufficiently slow to allow of a number of measurements being made with any one solution—a condition that is satisfied by very few inorganic salts—it was thought worth while to make a somewhat extended study of the hydrolysis of this salt under different conditions as to (1) dilution; (2) the presence of other chlorides and neutral salts; (3) the reversibility of the reaction.

Previous Observations regarding this Hydrolysis.

The action of light on potassium platinichloride appears to have been first noted by Sonstadt (P., 1898, **14**, 25). He states that light has the same effect on very dilute solutions of the salt as heat. A solution containing 1 part of salt in 10,000 parts of water became turbid when heated for an hour or two. He observed no effect in the case of more concentrated solutions, and seems to have judged the extent of the reaction from the appearance of the solution and the formation of a sediment, considered to be platinum monochloride.

It is of interest here to refer to a letter of Sir John Herschel to Dr. Daubeny, written in 1832 (*Phil. Mag.*, 1832, [iii], **1**, 58). This letter states that if a solution of platinum in nitromuriatic acid, in which the excess of acid has been neutralised by the addition of lime, this being followed by filtration, is mixed with water in the dark, no precipitation takes place for a very long while, but if the mixture is exposed to sunlight it instantly becomes milky and a copious precipitate forms. The writer of the letter further showed that this effect was confined to the violet end of the spectrum, no action taking place when tubes containing the

platinum solutions were immersed in red- or yellow-coloured solutions and then exposed to the sunlight.

That light greatly accelerates the hydrolytic decomposition of platinum tetrachloride seems to have been generally recognised. Kohlrausch found that the conductivity of aqueous solutions of this compound increased much more rapidly when under the influence of light than when kept in the dark. The presence of the platinum electrodes also increased the velocity of the reaction. Solutions of chloroplatinic acid more concentrated than $N/10$ were apparently not affected by light.

Experimental.

Preparation of Materials.

Hydrochloric Acid.—The hydrochloric acid used was prepared by heating concentrated hydrochloric acid and passing the liberated gas into distilled water, the first and last parts of the distillate being rejected.

Potassium Chloride.—Commercial potassium chloride was recrystallised several times from water saturated with hydrogen chloride, finally from pure water. Portions so obtained were washed free of mother liquor and dried at a high temperature.

Potassium Platinichloride.—In preparing the chloroplatinic acid from which the platinichloride was obtained, platinum scrap was freed of surface impurities, then boiled for some time in concentrated hydrochloric acid. The platinum was then dissolved in aqua regia and the solution evaporated almost to dryness, after adding concentrated hydrochloric acid. After again adding hydrochloric acid and evaporating a second time, the residue was dissolved in water containing hydrochloric acid, and the platinum precipitated from this by adding a solution of ammonium chloride. The resulting ammonium platinichloride was collected in a Gooch filter, washed with alcohol and water, and dried in an air-bath at a low temperature. The dry salt was then reduced by heating in a current of hydrogen, and the platinum-black formed was well washed in water.

In order to ensure the absence of any nitric acid from the final preparation, the platinum-black was dissolved according to the method suggested by Weber (*J. Amer. Chem. Soc.*, 1908, **30**, 29) and modified by the author (*Zeitsch. anorg. Chem.*, 1910, **66**, 169). According to this method, the platinum-black is made the anode in the lower part of a glass tube, about 2 cm. in diameter, containing concentrated hydrochloric acid as electrolyte. At the anode the chlorine attacks the platinum, forming platinum chloride, and the resulting chloroplatinic acid falls to the bottom and can

be drawn off through a siphon sealed to the bottom of the main tube. The solution prepared in this way is somewhat diluted, and the platinum then precipitated by adding slowly a solution of a portion of the purified potassium chloride. The precipitated platinichloride, after being washed and dried, is ready for use.

Apparatus.

The graduations on the pipettes and burettes were tested by weighing the water delivered, allowance being made for air-displacement and the temperature of the water. In the case of the flasks, a graduation mark was made at that point on the stem at which the flask contained water sufficient to balance brass weights equal to the apparent weight of a kilogram or 100 grams, as the case might be, of water weighed in air at 20°.

The weights were corrected by the method suggested by Richards (*J. Amer. Chem. Soc.*, 1900, **22**, 144).

Method of Measuring the Extent of the Hydrolytic Action.

As hydrochloric acid is formed as the hydrolysis proceeds, the rate at which the reaction takes place and the extent to which it has proceeded at any given time can be measured by titrating a known volume of the solution with a standard solution of an alkali, such as barium hydroxide. Among several indicators tried, such as methyl-red, methyl-orange, cochineal, and phenolphthalein, none appeared superior to phenolphthalein. The colour reaction with this substance was distinct and delicate. With the burettes employed in this work, the error in reading the volume delivered did not exceed 0·02 c.c., and this, with the strength of solution employed as standard, corresponded with 0·0000078 gram of hydrogen chloride.

The solutions first studied contained $\frac{K_2PtCl_6}{100} = 4{\cdot}864$ grams, $\frac{K_2PtCl_6}{200} = 2{\cdot}432$ grams, $\frac{K_2PtCl_6}{400} = 1{\cdot}216$ grams, and $\frac{K_2PtCl_6}{800} = 0{\cdot}6080$ gram of potassium platinichloride in a litre of solution. In terms of equivalent gram-molecules of platinum chloride they were, respectively, $N/25$, $N/50$, $N/100$, and $N/200$. These solutions were prepared by weighing the required amount of salt in each case; the necessary water was added in the dark, and the solution carefully protected from the light until everything was in readiness to begin a series of measurements. The velocity of the hydrolytic reaction was so low, even for the most concentrated solution studied, that the time required to dissolve the platinum salt need not be considered in any of the measurements. The

initial acidity was now measured—this was seldom equivalent to more than 0·05 c.c. of the standard for a 10·0 c.c. portion of the platinum solution. The vessels containing the solutions were then immersed in water-baths contained in glass tanks, and here exposed, at a certain distance, to the radiations from a 300-watt lamp. The temperature of the bath was maintained constant within 0·5° by means of a system of tubes, through which water circulated. An ammeter reading to 0·001 ampere was placed in series with the lamp, and by means of a voltmeter the energy being used was measured at frequent intervals. From time to time, 10 c.c. portions of the platinum solutions were withdrawn by means of a pipette, and the acidity was titrated against the standard alkali. The results obtained for the above four solutions are given below.

The figures in the first column indicate the time, in minutes, during which the solution has been exposed to the light. The second column shows the number of c.c. of alkali necessary to neutralise a 10 c.c. portion of the platinum solution. The third column contains the weight, in grams, of hydrogen chloride formed in 100 c.c. of solution.

Table I.

N/200-K_2PtCl_6 *Solution.*

Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
5	0·04	0·00015
20	0·10	0·00039
40	0·14	0·00054
65	0·20	0·00073
125	0·32	0·00125
215	0·54	0·00210
265	0·64	0·00249
400	1·08	0·00421
580	1·72	0·00671
945	2·34	0·00913
1736	3·06	0·01193
2200	3·30	0·01287
2900	3·35	0·01365

N/100-K_2PtCl_6 *Solution.*

Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
40	0·20	0·00078
125	0·40	0·00156
265	0·74	0·00288
410	1·34	0·00495
580	1·92	0·00749
955	3·00	0·01174
1455	3·96	0·01544
1810	4·14	0·01615
1900	4·20	0·01638
2150	4·24	0·01653
2750	4·29	0·01673

N/50-K_2PtCl_6 *Solution.*

Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
40	0·27	0·00105
60	0·32	0·00125
125	0·51	0·00199
240	0·84	0·00328
430	1·53	0·00597
1035	4·04	0·0158
1630	5·24	0·0204
1910	5·68	0·0222
2050	5·86	0·0229
2400	6·36	0·0248
2700	6·45	0·0252

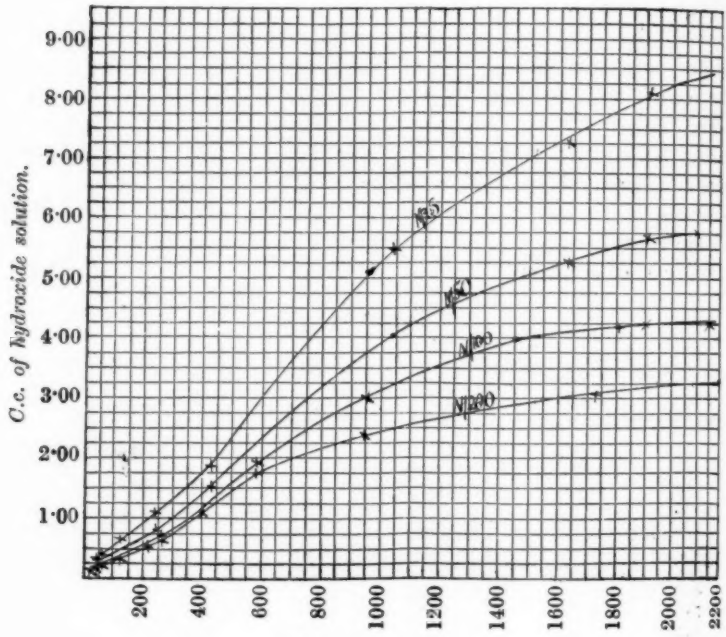
N/25-K_2PtCl_6 *Solution.*

Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
40	0·32	0·00125
60	0·42	0·00164
125	0·68	0·00265
240	1·10	0·00429
430	1·88	0·00733
1035	5·46	0·0213
1630	7·24	0·0282
1910	8·12	0·0317
2280	8·56	0·0334
2600	8·70	0·0339

These results show that the different solutions reach a condition of equilibrium in almost the same time. The $N/200$-solution attains a condition of maximum acidity some two or three hours after the most concentrated one.

If we calculate the percentage of chlorine that has been set free from the platinum salt when equilibrium has been reached, we find that for the four solutions the values are, beginning with the most

FIG. 1.



dilute solution, 74·7, 45·8, 35·2, and 23·2 per cent. of the chlorine present as platinic chloride.

The relationship between the time and the progress of the reaction is better shown by the curves of Fig. 1, where times are plotted as abscissæ against volumes of barium hydroxide solution used for the titration.

The first part of the curve shows nearly a straight line, that is, during the period that the first three-fifths of the reaction is taking place, indicating that the hydrolysis goes on at an almost constant rate for a considerable period of time. A velocity-constant for this part of the reaction may then be calculated by dividing the

amount of hydrogen chloride formed by the time and multiplying by the dilution.

There is an indication in the case of the two weaker solutions of what Goodwin (*Zeitsch. physikal. Chem.*, 1896, **21**, 1) has termed an induction period, during which the reaction proceeds very slowly. This would suggest that some substance may be forming—a product of the reaction—that catalyses the reaction during its later stages. This point can be discussed to better advantage when considering the reaction that takes place in the dark.

In order to show that the rate of the reaction is proportional to the intensity of the light for a given source of light, the following measurements were made for $N/100$- and $N/200$-solutions placed at a distance of 40 cm. from the source. The temperature and other factors were maintained the same as in the previous measurements.

$N/200$-*Solution at* 40 *cm.*

Time, minutes.	$Ba(OH)_2$ solution, c.c.
220	0·14
405	0·28
585	0·48
950	0·76
1741	1·44
2472	2·24
3195	2·56
4010	2·70
5135	2·84

$N/100$-*Solution at* 40 *cm.*

Time, minutes.	$Ba(OH)_2$ solution, c.c.
125	0·16
265	0·24
410	0·40
580	0·64
955	0·94
1455	1·68
1810	2·12
2370	2·92
3165	3·48

For the sake of comparison, we may set down opposite the volume of hydroxide solution necessary for the titration the time during which the solution was exposed; the corresponding time for the solutions exposed at 20 cm. distance is also shown in the table, these values being taken from the curves of Fig. 1.

TABLE III.

$Ba(OH)_2$ solution, c.c.	Time of exposure for solution $N/200$, minutes. At 20 cm.	At 40 cm.	$Ba(CH)_2$ solution, c.c.	Time of exposure for solution $N/100$, minutes. At 20 cm.	At 40 cm.
0·14	40	220	0·16	35	125
0·28	100	405	0·24	50	265
0·48	188	585	0·40	125	410
0·76	300	950	0·64	205	580
1·44	510	1741	0·94	315	955
2·24	870	2472	1·68	515	1455
2·56	1125	3195	2·12	640	1810
2·70	1280	4010	2·92	925	2370
2·84	1460	5135	3·48	1175	3165
2·92	1555	5665	4·00	1500	4105
			4·16	1860	6685

These results show that at the beginning of the hydrolysis the rate of the reaction is approximately proportional to the intensity of the light. However, after the reaction has proceeded a certain distance—when about one-tenth of the total amount of hydrogen chloride has been formed—the rate of the reaction for the solution at the greater distance is more rapid than the intensity law would predict. This is perhaps to be expected if the later stages of the reaction are influenced by a product formed during the hydrolysis. It is worth noting that this change in rate occurs when practically the same amount of hydrogen chloride has been formed in each solution. The final equilibrium point is apparently not affected by a change in the intensity of the light, as the titration is almost identical in the two cases.

It will be of interest to record at this point the behaviour of solutions of the platinichloride when made up and kept in the dark. The solutions were protected from the light by wrapping the container in black paper and then enclosing it in a thick wooden box, blackened within and without. The following tables will show the results of these observations. In the preparation of the $N/25$-solution the water had been very carefully distilled, and boiled again just before using. The salt had been kept in the dark for several days before making up the solutions, and every precaution was taken to exclude light, both while preparing the solutions and after.

The volumes of solution and weights of hydrogen chloride are expressed in the units used before.

TABLE IV.

$N/25$-K_2PtCl_6 *in Darkness.*

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Grams.
68·3	0·06	0·00023
162·0	0·12	0·00047
354·0	0·28	0·00110
546·0	0·60	0·00236
937·0	1·52	0·00592
1120·0	2·04	0·00796
1440·0	3·04	0·01185
1775·0	4·94	0·01927
2177·0	7·14	0·02785
2515·0	8·13	0·0317
2735·0	8·46	0·0330
3090·0	8·65	0·0337

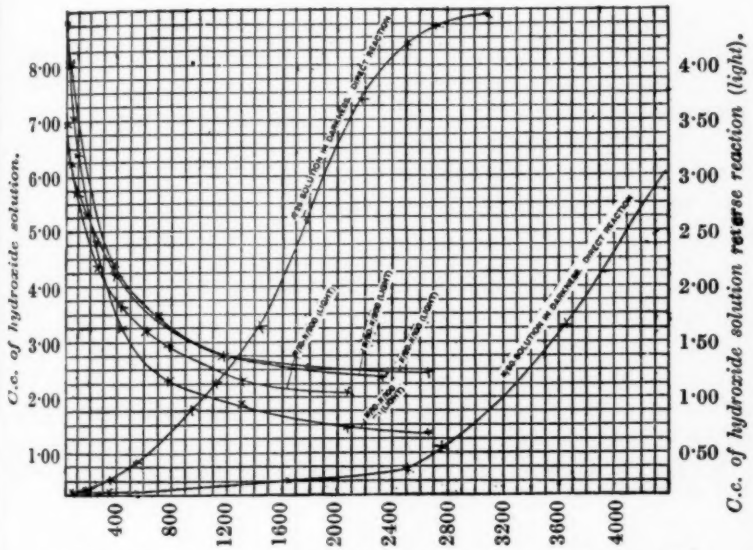
$N/50$-K_2PtCl_6 *in Darkness.*

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
68·3	0·04	0·00016
162·0	0·04	0·00016
354·0	0·04	0·00016
546·0	0·04	0·00016
1625·0	0·28	0·00110
2455·0	0·44	0·00173
2755·0	0·84	0·00330
3662·0	1·54	0·01177
4850·0	6·04	0·02355

In the case of the $N/100$- and $N/200$-solutions, there was no indication that hydrolysis had even started after they had been in the dark for six months. For the $N/25$- and $N/50$-solutions, the

results were as indicated. In the latter case, the hydrolysis had not proceeded far enough to be measured until approximately thirty days had elapsed. For the $N/25$-solution, the reaction had proceeded to such an extent that it could be detected at the end of five days. The curves of Fig. 2, obtained by plotting the results of table IV, show much more distinctly the character of the "induction" period. This period becomes more extended and exaggerated as the solution becomes more dilute, until, for a solution as dilute as $N/100$, no hydrolytic decomposition whatever takes place over as extended a period as six months. It appears

FIG. 2.



Time in minutes for reaction in light, in hours for reaction in dark.

strange, perhaps, that the more dilute solutions are the more stable. The concentration of the hydrogen and hydroxyl ions has evidently little to do with the progress of the reaction, although it might be argued that these factors are practically constant for the different solutions, the proportion of water to salt being so large for all concentrations studied.

The time required for the $N/25$-solution to reach an equilibrium point in darkness is approximately one hundred times as long as when exposed to the radiations of the 300-watt lamp. For the $N/50$-solutions, the difference in time is somewhat greater.

It seems possible that for the more concentrated solutions a

sufficient, although perhaps an exceedingly small, amount of some substance—perhaps an hydroxy-salt—is produced when the salt is first dissolved to catalyse the hydrolytic reaction, and, in the case of the $N/25$-solution, to give the reaction an appreciable velocity almost at the beginning. The shape of the curves of Fig. 2 is then more easily understood. The steep parts show the accelerating effect of the catalyst, in the absence of any effective radiations, in a very striking way. For the more dilute solutions, this catalyst is not produced in concentrations high enough to affect the progress of the reaction.

The Reverse Reaction.

On testing the solutions to determine whether the reaction could be driven in the opposite direction, it was found that when potassium chloride, sodium chloride, or hydrochloric acid was added to a hydrolysed solution, the reaction proceeded in the opposite direction, either in the dark or in the light, the extent to which the reverse reaction took place depending, in the case of any one solution, on the amount of chloride that had been added. The rate at which the reverse reaction proceeded was very much slower in the dark than in the light, as measurements given below will show. The effect of platinum-black on the reaction was also studied, as set forth in the tables. For this purpose, a strip of platinum foil was covered electrolytically with platinum-black, and this strip, after being thoroughly washed, was immersed in the solution to be studied.

TABLE V.

Reverse Reactions in Light: $N/100$-K_2PtCl_6 Solution.

$N/10$-KCl.			$N/20$-KCl.		
Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.	Time, minute.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	4·29	0·0167	Initial	4·29	0·0167
65	3·40	0·0133	20	3·90	0·0152
95	3·08	0·0120	245	2·56	0·00998
255	2·28	0·0089	385	2·06	0·0080
430	1·50	0·0059	700	1·62	0·0063
620	1·16	0·00452	1175	1·26	0·0049
775	1·04	0·00436	1775	1·16	0·0045
1305	0·82	0·00320	2665	1·10	0·0043
2070	0·60	0·00234			
2660	0·56	0·00218			

TABLE V. (*continued*).

$N/200$-K_2PtCl_6 Solution.

$N/10$-KCl.			$N/20$-KCl.		
Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.	Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	3·35	0·0131	Initial	3·35	0·0131
65	2·86	0·0112	35	3·00	0·0117
95	2·74	0·0107	185	2·54	0·0099
255	2·06	0·0080	385	1·98	0·0077
430	1·70	0·0066	810	1·46	0·0057
620	1·48	0·0058	1205	1·24	0·0052
775	1·34	0·0052	1775	1·12	0·0044
1305	1·04	0·00405	2323	1·06	0·0041
2070	0·92	0·00359	4850	0·86	0·00335
4850	0·59	0·00230	5600	0·70	0·00273
5600	0·52	0·00203			

The reverse reaction is seen to take place at a comparatively rapid rate at the beginning, the amount of change being greater here, in a given time, than for the direct reaction. This is no doubt because the added salt has so greatly increased the concentration of the chlorine ion. Towards the end, however, the progress becomes very slow, with the result that the time required for the reverse action to go to completion is much greater than the time necessary for the hydrolysis to take place. In the case of the $N/200$-platinum solutions, the time required for the reverse reaction is much greater than for the $N/100$-solutions.

The latter stage of the reaction for the $N/100$-potassium platinichloride–$N/10$-potassium chloride solution is complicated by the fact that, as the potassium platinichloride is regenerated, the solution becomes supersaturated with respect to this compound, and it crystallises out to a slight extent. This probably explains the crossing of the curves for the $N/10$-potassium chloride solutions, as shown in Fig. 2. This also goes to show that the hydrolysed salt is slightly more soluble in potassium chloride solutions than the normal compound.

If the rate of the reverse reaction is expressed according to the usual formula, using the results of the measurements, say, for the $N/200$-potassium platinichloride–$N/10$-potassium chloride solution, a constant is not obtained. The expression for a unimolecular reaction gives a value which continually diminishes, whilst the bimolecular formula yields a continually increasing number.

The results of measurements made on solutions reacting in the reverse direction in the dark are shown below in table VI. The effect of the addition of sodium chloride to the hydrolysed solution is also shown.

Table VI.

Reverse Reactions in Darkness.

Potassium Chloride Added.

$N/50$-K_2PtCl_6. $N/20$-KCl.

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	6·60	0·0257
1·50	5·32	0·0208
19·58	4·98	0·0194
73·50	4·32	0·0169
260·50	3·34	0·0130
601·50	2·80	0·0109
1101·5	2·38	0·0093
1657·0	2·10	0·0082
2540·0	1·84	0·0072
3096·0	1·80	0·0070

$N/200$-K_2PtCl_6. $N/10$-KCl.

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	3·35	0·0131
4·25	3·22	0·0126
49·25	2·60	0·0102
317·0	1·98	0·0077
1973·0	1·10	0·0043
3797·0	0·90	0·00351
5957·0	0·72	0·00281
8693·0	0·52	0·00203

$N/200$-K_2PtCl_6. $N/20$-KCl.

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	3·35	0·0131
49·25	2·78	0·0108
317·0	2·22	0·0087
1973·0	1·32	0·00515
3797·0	1·12	0·00437
5957·0	0·92	0·00359
8693·0	0·74	0·00289

Sodium Chloride Added.

$N/200$-K_2PtCl_6. $N/10$-NaCl.

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	3·35	0·0131
48	2·62	0·0102
75	2·42	0·0094
1732	1·34	0·0052
3556	1·10	0·00429
5716	0·86	0·00335
8452	0·50	0·00195
12300	0·29	0·00109

$N/200$-K_2PtCl_6. $N/20$-NaCl.

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	3·35	0·0131
48	2·94	0·0115
76	2·82	0·0110
—	—	—
3556	2·16	0·0084
5716	1·80	0·0070
8452	1·72	0·0067
16828	1·50	0·0059
20476	1·20	0·0047

$N/100$-K_2PtCl_6. $N/10$-NaCl.

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	4·29	0·0167
29	3·98	0·0155
219	3·42	0·0133
1296	2·52	0·0098
2376	2·16	0·0084
4488	1·68	0·00655

These results show that the reverse reaction, brought about by the addition of a soluble chloride to the hydrolysed solution, continues in the absence of light until, for the more concentrated solutions, much the same equilibrium point is reached as in the case of the same reaction taking place in the light. For the more dilute solutions, the latter equilibrium point is past, the reaction continuing for approximately two years, by which time the hydrolysis has almost disappeared.

The catalytic effect of platinum-black on the reverse reaction is shown by the results set forth below. In the first case, the solutions were exposed to the radiations from the 300-watt lamp, whilst the second series of results refers to the reaction taking place in the absence of light. In each case, these reactions were studied simultaneously with solutions kept under exactly the same conditions, except that no platinum-black was present.

TABLE VII.

Reverse Reactions with and without Platinum-black.

In Light.

$N/100$-K_2PtCl_6. $N/20$-KCl.

	With Platinum-black.		Without Platinum-black.	
Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	4·29	0·0167	4·29	0·0167
20	3·90	0·0152	3·90	0·0152
245	2·56	0·0100	2·56	0·0100
385	2·06	0·0080	2·06	0·0080
700	1·62	0·0062	1·62	0·0063
1175	1·26	0·0049	1·26	0·0049
1775	1·16	0·0045	1·16	0·0045
2665	1·10	0·0043	1·10	0·0043

In Darkness.

$N/100$-K_2PtCl_6. $N/20$-KCl.

	With Platinum-black.		Without Platinum-black.	
Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	4·29	0·0167	4·29	0·0167
28·75	3·72	0·0145	3·88	0·0151
219·7	2·84	0·0111	3·52	0·0137
1296·0	1·80	0·0070	2·36	0·0092
2376·0	1·36	0·0053	2·02	0·0079
4488·0	1·14	0·0045	1·54	0·0060
8376·0	1·02	0·0040	1·30	0·0051

It is apparent that the effect of the platinum-black is not great enough to show when the reaction is taking place at a relatively rapid rate before the lamp, but it is quite noticeable when the reaction is proceeding slowly in the dark.

A few results will show the effect of the presence of a neutral salt, such as potassium nitrate, in the solution undergoing hydrolysis. The values from measurements of two solutions are given.

TABLE VIII.

Direct Reaction with Potassium Nitrate.

$N/200$-K_2PtCl_6. $N/20$-KNO_3.			$N/200$-K_2PtCl. $N/10$-KNO_3.		
Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.	Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	0·00	—	Initial	0·00	0·0000
100	0·20	0·00078	100	0·22	0·00086
175	0·40	0·00156	190	0·46	0·00179
350	0·78	0·00304	225	0·58	0·00226
465	1·00	0·00390	315	0·84	0·00328
665	1·44	0·00562	605	1·52	0·00592
850	1·86	0·00725	800	1·91	0·00745
1380	2·66	0·0104	1215	2·40	0·00936
1775	2·92	0·0114	1775	2·90	0·0113
2020	3·04	0·0119	2020	3·08	0·0120
2650	3·28	0·0128	2650	3·26	0·0127
3000	3·44	0·0134	3000	3·40	0·0133

These results show that whilst the potassium nitrate has a retarding effect at the beginning of the reaction, the acidity of the solution finally reaches just as high a value as in the absence of the neutral salt. The total time required for the reaction to reach an equilibrium point is but slightly greater when the potassium nitrate is present. In agreement with the retarding effect of the nitrate is the fact that the solution which contains the greater amount of neutral salt lags slightly behind the other.

As stated above, it appears from the results in table I that a substance may be formed from the hydrolysis which acts as a catalyst of the reaction, increasing the speed very perceptibly during the first half of the decomposition. This point was further tested, as follows. Two solutions were prepared in the same manner, of equal concentration as regards platinum salt, whilst one contained 1 c.c. of dilute hydrochloric acid. They were then exposed at the same temperature and at the same time to the radiations from the lamp, at equal distances from the source. Measurements of the acidity of the solutions were then made at frequent intervals. The results failed to show any accelerating influence whatever on the part of the hydrochloric acid. The

reaction necessarily did not proceed so far in the solution containing the added chlorine ions, but this was the only effect noticed.

Another experiment with the same object in view was made, as follows. Two solution of the platinum salt were prepared, one $N/100$, the other $N/400$. These were exposed to the light until partly hydrolysed, then placed in the dark. The acidity of the more concentrated solution was measured after twenty days, and the measurement showed that the hydrolytic reaction had continued until the usual equilibrium point had been reached. In the case of the $N/400$-solution, a measurement was made after thirty days, but the rise in acidity, if any, was so small that it could not be detected with certainty. After thirty-eight days more, the result of another measurement indicated that the hydrolysis was proceeding, but very slowly. A 10 c.c. portion, which neutralised 0·88 c.c. of alkaline solution when first placed in the dark, now required 0·98 c.c. The next two months brought no perceptible change in this solution, and sixteen months after it had been placed in the dark a 10 c.c. portion required only 1·10 c.c. of hydroxide solution. Another $N/400$-solution, made up at the same time as this one, but never exposed to the light, showed no indication of any hydrolytic action after sixteen months. It would seem as if a certain concentration of the catalytic reagent was necessary before the hydrolysis will proceed. In the case of the $N/400$-solution that had been exposed to the light, this concentration had apparently just been reached before the solution was placed in the dark.

It was not expected that the accelerating influence of platinum-black would be sufficiently great to be noticed in a solution undergoing hydrolysis before the light. It was thought worth while, however, to measure this effect on solutions reacting in the dark. Accordingly, two solutions were carefully prepared, each $N/25$. In one was placed 0·05 gram of platinum-black. Both solutions were placed in the dark and measured from day to day. After three days, 10 c.c. of one solution neutralised 0·06 of alkali solution, whilst the same volume of the one containing the platinum-black required 0·25 c.c. After five days, the corresponding volumes of alkali solution were 0·06 c.c. and 0·45 c.c. The effect of the platinum-black was very evident both in starting the hydrolysis and in accelerating the reaction.

Another experiment, almost identical with this one, was made by adding 5 c.c. of an $N/25$-solution completely hydrolysed to a newly prepared $N/100$-solution, and placing this in the dark. The reading for a 10 c.c. portion of this solution was now 0·98 c.c. of alkali; after two months, the volume of alkali required for a 10 c.c. portion was 2·32 c.c., showing that a sufficient amount of

the accelerating substance had been added to cause the hydrolysis to take place.

The effect of the temperature on the rate of the reaction and the extent of the hydrolysis received some attention. It was first ascertained whether a solution which would not undergo hydrolysis in the dark at the ordinary temperature would hydrolyse if kept at 80°. An $N/100$-solution was tested in this way. The titration for a 10 c.c. portion of this solution was 0·04 c.c. at 20°. After being kept in the dark at 80° for three hours, the corresponding titration was 0·16 c.c. On cooling to 20°, still in the dark, the titration fell to 0·08 c.c. After being kept in the dark at 80° for another period of three hours, a 10·0 c.c. portion again required 0·16 c.c. of alkali. In the absence of light, the temperature has little, if any, influence on the hydrolysis. The same conclusion is drawn from a comparison of the rate of the reaction taking place at 25° with that at 35°. The variation here is only manifest toward the end of the reaction, when the difference in the equilibrium point—a greater degree of hydrolysis at the higher temperature—is sufficient to show in the final readings.

For the purpose of ascertaining to what extent the hydrolysis would be increased by a rise in temperature, three solutions were exposed to the radiations of the 300-watt lamp at a distance of 20 cm., the water-bath being maintained at the temperature shown below. From time to time, 10 c.c. portions of the platinum solutions were withdrawn and titrated, the light being continued at any one temperature until equilibrium had been attained.

TABLE IX.

Effect of Temperature on the Hydrolysis.

	$N/100$-K_2PtCl_6.		$N/50$-K_2PtCl_6.		$N/25$-K_2PtCl_6.	
Temperature.	$Ba(OH)_2$ solution, c.c.	HCl (100 c.c.). Gram.	$Ba(OH)_2$ solution, c.c.	HCl (100 c.c.). Gram.	$Ba(OH)_2$ solution, c.c.	HCl (100 c.c.). Gram.
20°	4·29	+0·0167	6·45	+0·0252	8·70	+0·0339
50	5·24	+0·0204	7·45	+0·0291	10·16	+0·0396
80	5·90	+0·0230	8·20	+0·0319	11·06	+0·0431

If we express the increase in the acidity of these solutions as percentages of the values at 20° we obtain the following coefficients for temperatures between 20° and 80°: $N/100$ 0·62, $N/50$ 0·45, $N/25$ 0·45 per cent.

These coefficients are not very different for the several concentrations studied. From the amount of hydrogen chloride formed at 80°, we find that for the $N/100$-solution 63 per cent. of the

chlorine present as platinic chloride has been used to form hydrogen chloride.

If we represent by chemical equations the several stages of the hydrolytic decomposition of the platinum salt, we find that for the $N/25$-solution the equation

$$K_2PtCl_6 + H_2O = 2K^{\cdot} + PtCl_5(OH)'' + H^{\cdot} + Cl'$$

indicates pretty closely the extent to which the hydrolysis has taken place, whilst for the $N/50$-solution the expression

$$2K_2PtCl_6 + 3H_2O = 4K^{\cdot} + PtCl_5(OH)'' + PtCl_4(OH)'' + 3H^{\cdot} + 3Cl'$$

would represent more nearly the condition of the solution. When the solutions are as dilute as $N/100$ or $N/200$, the respective equations would be

$$K_2PtCl_6 + 2H_2O = 2K^{\cdot} + PtCl_4(OH)_2'' + 2H^{\cdot} + 2Cl^{\cdot}$$

and

$$K_2PtCl_6 + 3H_2O = 2K^{\cdot} + PtCl_3(OH)_3'' + 3H^{\cdot} + 3Cl'.$$

The above equations correspond with a temperature of 20°. At higher temperatures, the decomposition of the salt is more nearly complete, which is in agreement with the fact that when a dilute solution of the platinichloride is boiled in the light, an insoluble substance is deposited.

Obviously the possibilities of this hydrolytic action should be kept in mind when making a determination of potassium by means of this salt; if a solution of the platinichloride is being evaporated, a sufficient amount of hydrochloric acid must be present to prevent the hydrolysis taking place, whilst if the salt is being precipitated, hydrochloric acid must again be present to ensure the formation of the normal compound.

Potassium platinibromide shows some interesting features not noticeable in the case of the platinichloride, and it is hoped to submit soon a communication dealing with this compound.

Summary.

It has been shown that solutions of potassium platinichloride undergo hydrolysis when exposed to the action of light.

If the solution is as concentrated as $N/50$, this hydrolysis will begin and will be completed in the dark; for a $N/100$-solution or one more dilute, no decomposition takes place when light is excluded.

A substance is formed by the hydrolysis which catalyses the reaction, and will initiate the decomposition in a newly prepared solution.

The addition of a soluble chloride to the hydrolysed solution

causes a complete reversal of the reaction, showing that the substances formed during the direct reaction are soluble.

The reverse reaction is influenced by light in much the same way as the direct. The complete reversal of a solution as dilute as $N/200$ requires nearly two years.

A neutral salt has a slight retarding effect on the direct reaction, but does not influence the equilibrium point.

The accelerating influence of platinum-black on both the direct and reverse reactions is quite noticeable when these reactions are taking place in the dark, but is not measurable when light is acting on the solutions.

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CXXVI.—*Studies in Catalysis. Part XIV. The Mechanism of the Inversion of Sucrose.*

By CATHERINE MARGARET JONES and WILLIAM CUDMORE MCCULLAGH LEWIS.

IN connexion with the investigations carried out in this laboratory on the chemical reactivity of molecular and ionic species from the point of view of the radiation hypothesis, it was found necessary, in one section of the work, to make a series of determinations of velocity-constants in the case of a few familiar reactions, such as the inversion of sucrose, with the object of studying more particularly the influence of change of environment on the rate of the reaction. The principle of mass action, in its usual formulation, affords no information of an a priori kind regarding the effect of environment. It is hoped that the radiation hypothesis may be of assistance in this connexion (compare Lewis, *Scientia*, 1919, **25**). As a preliminary, it is necessary to possess as clear a view as possible of the actual material mechanism of the selected reaction in order to be able to proceed with some degree of confidence to the further problems involved in alterations of material and temperature environment. The inversion of sucrose is a reaction particularly suitable for the purpose in view in so far as precision of measurement is concerned. Further, this reaction has been frequently investigated, but, in spite of this, the inversion process

obviously requires further investigation, more particularly as regards the way in which the hydrogen ion enters into the process.

The present research was undertaken primarily for this purpose. As will be seen, the experimental measurements consist on the one hand of determinations of reaction velocities, and on the other of determinations of the average (geometric mean) activities of the hydrogen ions, obtained by the electrometric method. In agreement with the conclusion already reached by Harned (*J. Amer. Chem. Soc.*, 1918, **40**, 1461) in connexion with other reactions catalysed by ions, it has been found that the activity of the hydrogen ion, as defined by G. N. Lewis, is the determining factor for the rate of the reaction. This conclusion is of great importance, as it not only includes to a certain extent the phenomenon known as the solvent displacement effect, but also, as pointed out by Harned, appears to exclude the necessity of ascribing any catalytic influence to the undissociated molecule of the acid. In order to obtain data which could be employed for various kinds of calculation, care has been taken to determine the amounts of all constituents, water included, in known volumes of the various solutions.

As will be shown later, the most probable material mechanism of the inversion reaction is that expressed by $RH^{\cdot} + H_2O \longrightarrow$ dextrose + lævulose. That is, the reaction is a true bimolecular one, between a molecule of water and a complex ion, formed by the addition of hydrogen ion to the sucrose molecule.

Experimental.

Reaction Velocity Measurements.

The rate of inversion of sucrose was carried out in the ordinary manner with the usual precautions at 20°, 30°, 40°, and 50° in the presence of $N/10$-sulphuric acid, the initial concentration of sucrose being varied over a wide range, namely, from 10 to 70 per cent., in order to bring into prominence any effect produced by the displacement of the solvent, water, the volume of the various solutions being maintained constant. All determinations were carried out in duplicate, and satisfactory unimolecular velocity-constants were obtained throughout the entire range examined. To save space, the mean values only of the observed velocity-constants, referred to the base e and in seconds $^{-1}$, as well as the initial concentrations of sucrose and water, are given in the following table.

TABLE I.

Catalyst: 0·1*N*-H_2SO_4.

Grams of sucrose in 100 c.c. of solution.	Gram-molecules of water ($M=18$) per litre.	Unimolecular velocity-constant.			
		$\times 10^6$ at 20°.	$\times 10^5$ at 30°.	$\times 10^5$ at 40°.	$\times 10^4$ at 50°.
10	51·95	4·43	1·83	6·73	2·29
20	48·45	4·79	1·97	7·37	2·55
30	44·99	5·21	2·12	8·04	2·81
40	41·62	5·54	2·29	8·80	3·08
50	38·09	5·95	2·45	9·53	—
60	34·59	6·22	2·58	10·22	—
70	30·94	6·29	2·66	10·92	3·94

It will be observed that in all cases displacement of the water by the sucrose causes a definite increase in the velocity-constant, a further illustration of the anti-catalytic effect of water already observed in other reactions, for example, hydrolysis of esters. If the reaction is a true bimolecular one, it is necessary to divide the velocity-constants by the corresponding concentration of water in order to obtain comparable quantities in so far as this stoicheiometric correction is concerned. Whether the observed velocity-constants require to be thus divided or not, it is possible to obtain values for the critical increment, E, by means of the equation $d \log k/dT = E/RT^2$, from the velocity-constants at different temperatures. It was thus found that with an increasing initial concentration of sucrose, the value of E rises steadily over all three ranges of temperature investigated, namely, 20° to 30°, 30° to 40°, and 40° to 50°. That is, the critical increment (or the temperature-coefficient) apparently rises, whilst the velocity-constant itself also increases. As this is in direct contradiction to the conclusion already drawn, namely, that the greater the critical increment the smaller, *ceteris paribus*, the velocity-constant, it was concluded that the catalytic conditions were not comparable at any pair of temperatures, as the content of sucrose was varied. The behaviour, in fact, could be accounted for on the assumptions that (*a*) the catalytic influence of the acid at any given temperature increases with increasing concentration of sucrose, and (*b*) that this increase in catalytic activity is greater the higher the temperature. This conclusion did not appear to be a very probable one on the basis of the degree of electrolytic dissociation of the acid, for in the case of sulphuric acid the catalytic effect ascribed to the undissociated molecule is approximately the same as that of the hydrogen ion, and in general the ratio of the catalytic effect ascribed to the molecule to that of the ion decreases as the temperature increases. Owing to the large viscosity effects produced by a variation in the

concentration of sucrose, electrical conductivity measurements could not give direct information, even assuming that the original equation of Arrhenius was valid, an assumption which has recently been called in question. On this account, it was decided to determine the activity or thermodynamic concentration of the hydrogen ions (strictly speaking, the geometric mean of the activity of hydrion and HSO_4') by means of electromotive-force measurements.

Activity of Hydrogen Ion in Aqueous Solutions of Sucrose.

The cell employed was of the following type:

Hydrogen electrode	H_2SO_4 + sucrose $0{\cdot}1N$	saturated KCl	normal calomel electrode

The use of a saturated solution of potassium chloride as a middle liquid, to eliminate contact potential differences, has been frequently recommended (compare Fales and Vosburgh, *J. Amer. Chem. Soc.*, 1918, **40**, 1291). The absolute value of the normal calomel electrode was taken to be $+0{\cdot}56$ volt at 18°. Using T. W. Richards' value for the temperature-coefficient of this electrode, namely, 0·0006 volt per degree, the potential difference of the calomel electrode at 20° was taken to be 0·5612 volt, at 40° 0·5732 volt. The value of π_H, the potential of the hydrogen electrode in the sulphuric acid–sucrose solutions, was obtained by means of the following equations:

$$\pi_H = 0{\cdot}277 + 0{\cdot}058 \log_{10} H^{\cdot} \text{ at } 20°$$

and

$$\pi_H = 0{\cdot}296 + 0{\cdot}062 \log_{10} H^{\cdot} \text{ at } 40°,$$

where the electrolytic potential of hydrogen has been assumed to vary directly as the absolute temperature. The absolute value may not be correct on this basis, but as the quantity involved is a constant at any given temperature, the relative values of π_H at two different temperatures are comparable.

Table II contains the *E.M.F.* data obtained at 20°, the last column giving the average activity of the hydrogen ion expressed in gram-molecules per litre. Table III contains similar data for 40°. In all cases, dissolved oxygen was removed from the sucrose solutions to prevent any change in the sucrose in contact with the platinised platinum electrode.

TABLE II.

Temperature, 20°. 0·1*N*-H_2SO_4.

Grams of sucrose in 100 c.c of solution.	Gram-molecules of sucrose per litre.	Gram-molecules of water ($M = 18$) per litre.	*E.M.F.* of cell observed, in volts.	P.d. of hydrogen electrode, π_H.	Activity of hydrogen ion in gram-molecules per litre.
0	0	55·55	0·3555	0·2057	0·060
10	0·292	51·95	0·3520	0·2092	0·068
20	0·585	48·45	0·3485	0·2127	0·078
30	0·877	44·99	0·3450	0·2170	0·0895
40	1·169	41·62	0·3410	0·2202	0·105
50	1·460	38·09	0·3380	0·2282	0·118
60	1·755	34·59	0·3345	0·2267	0·139
70	2·047	30·94	0·3313	0·2299	0·162

TABLE III.

Temperature, 40°. 0·1*N*-H_2SO_4.

Grams of sucrose in 100 c.c. of solution.	*E.M.F.* of cell, in volts.	P.d. of hydrogen electrode.	Activity of H′ in gram-molecules per litre.
0	0·3580	0·2152	0·050
10	0·3545	0·2187	0·056
20	0·3522	0·2210	0·062
30	0·3460	0·2272	0·078
40	—	—	0·091*
50	0·3370	0·2362	0·109
60	—	—	0·130*
70	0·3280	0·2452	0·152

(Values marked with an asterisk are interpolated from the curve.)

It will be observed that the activity of the hydrogen ion is less at 40° than it is at 20°. This would be expected for the *concentration* of the ion, since the dissociation of the acid is accompanied by an evolution of heat.

The first conclusion to be drawn from the above data is that the activity of the hydrogen ion increases appreciably at both temperatures with an increase in the concentration of the sucrose, and further, as shown later in the figure, the rate of increase in activity is greater at 40° than it is at 20°. The bearing of these results on the velocity-constants will be considered in the next section.

The second conclusion is that the activity of an ion is related to its concentration in a very secondary manner. This has already been shown to be the case by several American investigators. The effect is well marked in the present instance. Thus, when the sucrose content is 70 per cent., the thermodynamic concentration of the hydrogen ion is 0·162 at 20° and 0·152 at 40°, although the

maximum actual concentration of hydrogen ion cannot exceed 0·10.

The third conclusion is that the displacement of the solvent by a non-electrolyte, sucrose, produces effects entirely analogous to those produced by addition of neutral salts, the addition of the sucrose, and consequent elimination of water, causing an increase in the activity of hydrogen ion from two- to three-fold. It is proposed to investigate this aspect of the displacement effect (compare Griffith and Lewis, T., 1916, **109**, 67) in further researches in this laboratory. The activity of ions in presence of a non-electrolyte appears to have been investigated in a single instance only, namely, by Harned (*J. Amer. Chem. Soc.*, 1915, **37**, 2467), who determined the activity of the hydrogen ion from hydrochloric acid, in the presence of mannitol, without observing, however, any marked effect over the concentration range employed.

The Probable Mechanism of the Inversion Process.

It was found that the directly observed velocity-constants (table I) at 20°, when divided by the concentration of the water and also by the corresponding activity of the hydrogen ion, gave a quantity which was a constant within the limit of the experimental error. Similarly, the data at 40° gave a constant independent of the sucrose or water content, the numerical value being, of course, greater than that at 20°. These constants represent bimolecular velocity-constants reduced to unit activity of hydrogen ions. The values are given in tables IV and V.

Table IV.

Temperature, 20°. 0·1*N*-H_2SO_4.

Grams of sucrose in 100 c.c. of solution.	Gram-molecules of water ($M=18$) per litre.	Unimolecular velocity-constant observed. $\times 10^6$.	Unimolecular velocity-constant divided by water concentration. $\times 10^6$.	Unimolecular velocity-constant $\times 10^6$ divided by water and also by activity of $H^{\cdot}$ ions.
0	55·55	4·14*	7·46*	1·24
10	51·95	4·43	8·53	1·25
20	48·45	4·79	9·88	1·27
30	44·99	5·21	11·58	1·29
40	41·62	5·54	13·31	1·27
50	38·09	5·95	15·61	1·32
60	34·59	6·22	17·97	1·29
70	30·94	6·29	20·33	1·25
			Mean =	$1·27\times10^{-6}$.

(Values marked with an asterisk are obtained by extrapolation.)

TABLE V.

Temperature, 40°. $0{\cdot}1N$-H_2SO_4.

Grams of sucrose in 100 c.c. of solution.	Gram-molecules of water per litre.	Unimolecular velocity-constant observed. $\times 10^5$.	Unimolecular velocity-constant divided by water concentration. $\times 10^6$.	Unimolecular velocity-constant divided by water and also by $H^\cdot$ activity. $\times 10^5$.
0	55·55	5·98*	1·08*	2·16
10	51·95	6·73	1·30	2·31
20	48·45	7·37	1·52	2·46?
30	44·99	8·04	1·79	2·30
40	41·62	8·80	2·11	2·31
50	38·09	9·53	2·50	2·30
60	34·59	10·22	2·96	2·27
70	30·94	10·92	3·53	2·33

Mean = $2{\cdot}305 \times 10^{-5}$.

(Values marked with an asterisk are obtained by extrapolation.)

The two mean values, $1{\cdot}27 \times 10^{-6}$ at 20° and $2{\cdot}305 \times 10^{-5}$ at 40°, represent the true bimolecular velocity-constant, k_{bi}, of the reaction, where k_{bi} is defined by

$$k_{bi} = k_{uni} / [H_2O] [H^\cdot],$$

where k_{uni} is the observed unimolecular velocity-constant, $[H_2O]$ the concentration of the water ($M = 18$), and $[H^\cdot]$ is the activity of the hydrogen ion. The values of k_{bi} as thus defined are independent of the concentration of sucrose or water, and also of the activity of the acid catalyst. The values of k_{bi} depend only on the temperature.

Since the change in the observed velocity-constant with the composition of the solution is entirely accounted for, after the introduction of the necessary stoicheiometric correction for water, by the activity of the hydrogen ion, it follows that the undissociated molecule of the acid possesses no catalytic effect in this case. This conclusion has already been drawn by Harned (*loc. cit.*) in other cases in the presence of neutral salts. It is hoped that further investigation with other acids will settle the question as to whether this conclusion is a general one for aqueous solutions. In the case of gaseous systems, catalysis by means of acid is scarcely known. De Hemptinne (*Zeitsch. physikal. Chem.*, 1892, **13**, 561) states that a positive catalytic effect is produced by hydrogen chloride gas in the hydrolysis of gaseous esters. In these circumstances, and probably therefore in non-ionising solvents, the undissociated molecule of the acid is the catalysing individual.

The fact that constant values for k_{bi}, as defined above, are

obtained at a given temperature, removes the difficulty already mentioned in connexion with the apparent variation of the critical increment with composition of the system. When the catalytic conditions are really made the same at two different temperatures, a single value for E, the critical increment per gram-molecule of sucrose inverted, is obtained, this value being independent of the concentration of sucrose or water in the system. The value of E calculated from k_{bi} at 20° and 40° is 26,390 calories. The accuracy of this value depends on the relative accuracy with which the activities of the hydrogen ions at 20° and 40° have been determined. This numerical value represents the sum of the critical increments of the reactants, which will be shown later to be the complex ion (sucrose $H^{\cdot}$) and water.

The constancy of k_{bi} may be employed as a criterion in attempting to determine the mechanism of the inversion process by means of stoicheiometric equations, for these equations must be such as to lead finally to an expression of the form

$$k_{bi} = k_{uni} / [H_2O] [H^{\cdot}].$$

Apart from this consideration, many alternative modes of expressing the inversion process suggest themselves. We shall consider five of the most probable of these, and show that only one of them is in agreement with the criterion. The latitude of choice arises from the doubt as to whether (*a*) the hydrogen ion which reacts is hydrated or not, (*b*) whether the sucrose which reacts is hydrated or not. The problem of hydration is one of the least satisfactory aspects of the theory of solutions, the evidence in most cases being conflicting.

Possibility 1.—Assume that practically all the sucrose is hydrated and that the same is true for the hydrogen ions, but that it is the non-hydrated sucrose which reacts with a hydrated hydrogen ion ($H_2O,H^{\cdot}$). Applying the law of mass action to the hydration of the sucrose, $R + H_2O = (R,H_2O)$, we have $K = [R,H_2O]/[R][H_2O]$, where K is the equilibrium constant of hydration and R stands for non-hydrated sucrose. The inversion process assumed to be correct is $R + (H_2O,H^{\cdot}) \longrightarrow$ dextrose + lævulose. Hence, rate of inversion = k_{bi} $[R][H_2O,H^{\cdot}]$. But rate of inversion = $k_{uni\ observed}[(R,H_2O)]$, since practically all the sucrose has been assumed to be hydrated. Hence,

$$k_{bi} = k_{uni}[(R,H_2O)]/[R][H_2O,H^{\cdot}] = k_{uni} \cdot K \cdot [H_2O]/[H_2O,H^{\cdot}].$$

This mechanism requires, therefore, that the product of the observed velocity-constant by the water concentration divided by the activity of the hydrogen ions should be a constant independent of the initial concentration of sucrose. This differs from the true

criterion, and, in fact, the right-hand side of the equation is not a constant. Hence, possibility 1 is incorrect.

Possibility 2.—Assume that practically all the sucrose is hydrated, but that the hydrogen ion is practically all unhydrated, and that the inversion process is $(R,H_2O) + H^+ \longrightarrow$ dextrose + lævulose. This leads finally to the conclusion that

$$k_{bi} = k_{uni} / [H^+].$$

The right-hand side of this expression is not constant. Hence, possibility 2 is incorrect.

Possibility 3.—Assume that practically all the sucrose is hydrated and that the hydrogen ion is also practically all hydrated, but that it is the non-hydrated hydrogen ion which reacts with hydrated sucrose, as in possibility 2. We have now to allow for K_i, the equilibrium constant of hydration of the ions,

$$K_i = [H_2O,H^+]/[H^+][H_2O].$$

This assumption leads finally to $k_{bi} = k_{uni} \cdot [H_2O] \cdot K_i \cdot /[H_2O,H^+]$, which is indistinguishable from possibility 1, and is therefore incorrect.

Possibility 4.—Assume that the sucrose and the hydrogen ions are practically all hydrated, and that it is the hydrated form of each which reacts according to the equation

$$(R,H_2O) + (H_2O,H^+) \longrightarrow \text{dextrose} + \text{lævulose}.$$

Then, $k_{bi} = k_{uni} /[H_2O,H^+]$, which, being equivalent to possibility 2, is incorrect.

Possibility 5.—Assume that the sucrose as well as the hydrogen ions is practically all non-hydrated, and that the first stage is addition to form a complex ion, thus: $R + H^+ = RH^+$, which is followed by the true inversion reaction,

$$RH^+ + H_2O \longrightarrow \text{dextrose} + \text{lævulose}.$$

We then have, rate of inversion $= k_{uni}' [R]$, also, rate of inversion $= k_{bi} \cdot [RH^+][H_2O]$, whence $k_{bi} = k_{uni} [R]/[RH^+][H_2O]$. Now, K_c the equilibrium constant of the complex-ion formation, is given by $K_c = [RH^+]/[R][H^+]$, whence $k_{bi} = k_{uni} / K_c \cdot [H_2O][H^+]$. This is in agreement with the criterion, the right-hand side being a constant, since it only differs from the criterion in containing the constant, K_c. It may be shown, further, that if the above mechanism is assumed, with the modification that the sucrose is nearly all hydrated, an expression is obtained which is not in agreement with the experimental result. Also, if possibility 5 is employed, with the modification that the ions are practically all hydrated, an equally incorrect expression is obtained. Finally, if possibility 5 is employed, with the modification that both sucrose and the ions are practically all hydrated, an incorrect expression is obtained.

It is reasonable to conclude, therefore, that possibility 5 as it stands is the only satisfactory mechanism.

The two stoicheiometric equations which express the inversion process are therefore:

$$R + H^{\cdot} = RH^{\cdot} \text{ (practically instantaneous)} \quad . \quad . \quad (1)$$

and

$$RH^{\cdot} + H_2O = \text{dextrose} + \text{lævulose (measurable)} \quad . \quad . \quad (2)$$

It is obvious that this mechanism accounts for the fact that the hydrogen ion is necessary in order that inversion may proceed with measurable speed. There is also some evidence of a preliminary nature for the existence of an addition complex of sucrose and hydrogen ion, which it is hoped may be communicated in detail later.

The mechanism of the inversion process to which we have been led involves equations (1) and (2), and also the assumption that the hydrogen ions and the sucrose molecules are not appreciably hydrated in aqueous solution. This represents the simplest set of conditions, but the result is somewhat surprising. Sucrose is usually regarded as being heavily hydrated in solution. As already pointed out, however, such an assumption would not lead to the observed constancy of the quantity expressed in the final columns of tables IV and V.

Hydrogen-ion Activity as a Function of the Composition of the Solution.

Rosanoff (*J. Amer. Chem. Soc.*, 1913, **35**, 173) has suggested that the catalytic effect of a solvent may be expressed as an exponential function of the concentration of the solvent. A similar relation has been employed by Wilson (*ibid.*, 1920, **42**, 715) to account for the effect of neutral salts on the hydrogen ion, as determined by electrometric measurements. Wilson appears to regard the increase in concentration of the hydrogen ion in the presence of neutral salts as real. The effect, however, involves the activity, and not necessarily the concentration, of the ion. The analogy of the effect produced by the displacement of water by addition of sucrose to that produced by a neutral salt has already been mentioned.

In the conditions obtaining in the present investigation we deal with the simultaneous influence of sucrose and water, since by addition of one constituent a certain amount of the other is eliminated. Let us suppose that the activity of the hydrogen ion can be expressed by

$$[H^{\cdot}] = A \, . \, e^{(bR + b'W)} \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where R and W are the concentrations of sucrose and water respectively in gram-molecules per litre, b and b' are the catalytic environmental constants characteristic of sucrose and water, b is a positive, whilst b' is a negative, quantity.

When there is no sucrose present, W becomes W_0 (namely, 55·55 gram-molecules per litre) and H^* becomes H^*_0. We can thus re-write equation (3) in the form:

$$H^* = H^*_0 e^{\{bR - b'(W_0 - W)\}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

Hence,

$$\log_e H^* = \log_e H^*_0 + bR - b'(W_0 - W). \quad . \quad . \quad . \quad (4)$$

In the present case it happens that a straight line is obtained when the concentration of sucrose is plotted against the concentration of the water. Hence we can write $W = W_0 + pR$, where p is a negative constant having the value $-12{\cdot}1$, the sucrose and water being expressed in gram-molecules per litre. Equation (4) can therefore be written in the present case in the form

$$\log_e H^* = \log_e H^*_0 + (b + b'p)R \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or, alternatively,

$$\log_e H^* = \log_e H^*_0 + (b/p + b')(W - W_0) \quad . \quad . \quad . \quad (6)$$

Equations (5) and (6) are both linear, that is, they represent the observed behaviour of the activity of the hydrogen ion as a function of the composition of the mixture, as is shown in the figure (graphs C and D).

Hence equation (3) is justified in so far, at least, as it satisfies the above condition in the present case. From the experimental data the following mean values are obtained:

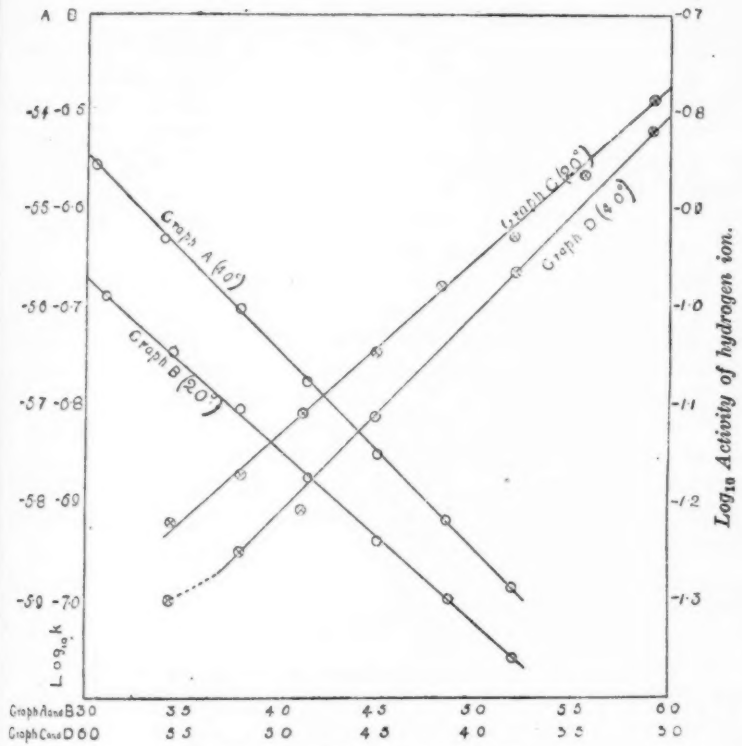
$$b - 12{\cdot}1b' = 0{\cdot}47 \text{ at } 20°,$$
$$b - 12{\cdot}1b' = 0{\cdot}56 \text{ „ } 40°.$$

It will be observed that equations (5) and (6), being equivalent, do not permit of a calculation of b and b' separately. Further experimental data involving a different functional relationship between the concentration of the sucrose and the water are required.

In equations (3) to (6) we have employed the most general type of formula, in which a possible catalytic effect has even been ascribed to the reactant solute, sucrose. In this connexion, there is an important consideration which has to be taken into account.

The observed unimolecular velocity-constants obtained at various temperatures are found to remain constant, within the limit of experimental error, throughout the entire course of the reaction. This is the case even when the initial concentration of sucrose is as high as 70 per cent., as is shown by the following results of duplicate experiments, which give the observed velocity-constants

obtained with 70 per cent. sucrose at 40° in the presence of $N/10$-sulphuric acid. The velocity-constant is calculated to the base e.



$$\left(k = \frac{\textit{observed velocity constant}}{\textit{water concentration}}\right)$$

TABLE VI.

Experiment 1.		Experiment 2.	
Time in seconds.	Unimolecular velocity constant × 10^5.	Time in seconds.	Unimolecular velocity constant × 10^5.
0	—	0	—
780	10·82	1200	10·81
1500	11·03	1950	10·81
2100	10·98	2460	10·83
3060	11·00	3060	10·77
3900	11·03	3960	10·89
5160	11·07	4440	10·86
6420	11·11	6360	10·96
7500	10·98	6900	10·97
	(55 per cent. of the sucrose decomposed.)		(53 per cent. of the sucrose decomposed.)

The fact that the velocity-constant does not alter indicates that the activity of the hydrogen ion is likewise sensibly constant. As, however, the concentration of the sucrose has diminished by more than one half, it follows that the environmental influence of the sucrose, if any, as measured by the quantity b, must be the same as that of the dextrose and lævulose formed as a result of the inversion. If these substances are inert, it would follow that $b=0$, and that therefore the environmental catalytic term b', characteristic of water, is $-0{\cdot}039$ at 20° and $-0{\cdot}046$ at 40°. The negative value indicates, of course, that the water is a negative catalyst for the process. The question of the absolute value of b will be dealt with in a later communication.

Returning to the graphs shown in the figure, it will be observed that with diminution in the concentration of water the curves for the hydrogen-ion activity at 20° and 40° are not parallel, but convergent. The same relation is exhibited by the curves for the velocity-constant shown in the same diagram, graphs *A* and *B*.

When the two sets of curves are combined, constant values for k_{bh}, as defined in the preceding section, are obtained. The relative positions of the two sets of curves afford the most direct evidence yet obtained for the conclusion that the activity of the ion completely determines the velocity of the reaction.

Summary.

(1) The velocity of inversion of sucrose in the presence of $N/10$-sulphuric acid has been determined at 20°, 30°, 40°, and 50°, the composition of the solution being altered by gradual displacement of the water by the sucrose. The velocity-constants vary with the initial composition of the mixture.

(2) The average activities of the hydrogen ion have been determined electrometrically in the various mixtures referred to in (1) at 20° and 40°. It is shown that the alteration in the velocity-constant can be accounted for completely by (*a*) allowing for the stoicheiometric correction for the water present, and (*b*) by allowing for the change in the activity of the hydrogen ions.

(3) In agreement with (2), the inversion process is shown to be bimolecular. It consists of two processes, (i) union of the non-hydrated hydrogen ion with a non-hydrated molecule of sucrose, thus, $R+H^{\cdot}=RH^{\cdot}$, this process being practically instantaneous, and (ii) the actual inversion reaction, $RH^{\cdot}+H_2O=$dextrose+lævulose. It is also concluded that the hydrogen ions and the sucrose molecules are not sensibly hydrated in aqueous solution.

(4) In agreement with Rosanoff's suggestion regarding the mode

of expressing the influence of solvent catalysts, the activity of the hydrogen ion is found to be an exponential function of the concentration of sucrose and water present.

(5) It is shown that the environmental catalytic influence of a molecule of sucrose, referred to in (4), is identical in magnitude with that exerted by one molecule of dextrose together with one molecule of lævulose.

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CXXVII.—*The Preparation of Guanidine by the Interaction of Dicyanodiamide and Ammonium Thiocyanate.*

By EMIL ALPHONSE WERNER and JAMES BELL.

BY heating a mixture of dicyanodiamide and ammonium chloride at 195° for ten minutes, Bamberger and Dieckmann (*Ber.*, 1892, **25**, 545) obtained diguanide, $C_2H_7N_5$. The yield was poor, and Ostrogovich (*Bul. Soc. Ştiinţe Bucureşti* 1910, **19**, 641), using ammonium iodide in place of the chloride, under similar conditions, obtained a much better result.

The reaction has been represented thus:

$$HN{:}C(NH_2)\cdot NH\cdot CN + NH_3\cdot HX = HN{:}C(NH_2)\cdot NH\cdot C(NH_2){:}NH,HX.$$

The dicyanodiamide complex is supposed to remain intact, whilst the cyanogen group unites with ammonia. On this assumption, the reaction is considered to uphold the cyanoguanidine formula for dicyanodiamide proposed by Bamberger (*Ber.*, 1883, **16**, 1459).

In the static condition, dicyanodiamide is stable up to 205°, when it melts, and is simultaneously depolymerised to cyanamide* and largely repolymerised to melamine (compare Werner, T., 1915, **107**, 715).

Several experiments have shown that dicyanodiamide is readily depolymerised to cyanamide at comparatively low temperatures in the presence of certain reagents, and its behaviour in the presence

* This fact is not referred to in the literature: if a gram or two of dicyanodiamide is heated to the melting point in a porcelain crucible and quickly covered with a glass bell-jar standing over a layer of water, the latter after a few moments will be found to give quite a copious yellow precipitate of silver cyanamide on addition of ammonio-silver nitrate solution.

of ammonium thiocyanate, for example, furnishes a case in point which is of practical value.

Pure guanidine thiocyanate has been easily prepared, in accordance with the equation

$$C_2H_4N_4 + 2NH_4{\cdot}SCN = 2CH_5N_3{\cdot}HSCN \quad . \quad . \quad . \quad (1)$$

Whilst the main change is equal to 90 per cent. of the theoretical, it is accompanied by a secondary reaction, whereby thioammeline is formed in small quantity. This does not interfere with the success of the preparation, as its separation from the chief product is a simple matter.

Pure dicyanodiamide was used in preliminary experiments to determine the best conditions, but from an economic point of view the commercial material may be conveniently employed.

The sample used in the following preparation contained dicyanodiamide = 95·5,* calcium carbonate = 3·25, melamine = 1·25 per cent.

An intimate mixture of 43·5 grams of dicyanodiamide (=42 grams, pure) and 76 grams of dry ammonium thiocyanate in coarse powder was heated in a tall, narrow beaker partly immersed in a glycerol-bath. A loose cardboard cover carried a thermometer, which served at the same time as a stirrer. At about 80°, the mixture began to melt; the temperature was gradually raised to 120°, about seventy minutes being required for the purpose, and this temperature was maintained for three and a-half hours. As the reaction proceeded, the product, which in the earlier stages was an almost clear liquid, gradually became very viscous. It was now treated, without previous cooling, with about 250 c.c. of water and allowed to digest until cold. After filtration and washing, 7·4 grams of amorphous residue were separated (residue *A*). The filtrate was concentrated as far as possible by evaporation at 100°, and the crystalline mass which formed on cooling weighed, when dry, 110 grams (Found: SCN = 47·76; guanidine thiocyanate requires SCN = 49·15 per cent.). The product was redissolved in about 200 c.c. of warm water, and 1·02 grams of amorphous solid (residue *B*) were separated by filtration.

The filtrate was evaporated to a syrupy consistency at 100°, and after "seeding" the cold solution with a minute crystal of guanidine thiocyanate, it quickly set to a crystalline mass of the pure salt (Found: SCN = 48·96 per cent.). The yield of pure

* A single recrystallisation of commercial crude dicyanodiamide is generally sufficient to obtain a product of this degree of purity. The material should be free from calcium hydroxide, which is occasionally present.

guanidine thiocyanate was 107·1 grams, equal to 90·8 per cent. of the theoretical.

The characteristic picrate was prepared as a means of identification. Whilst residue *A* contained the impurities originally present in the dicyanodiamide, 5·4 grams of pure thioammeline, $C_3H_5N_3S$, were separated from it by treatment with sodium hydroxide solution and precipitation, after filtration, by carbon dioxide. It was identified by its properties, as described by Klason (*J. pr. Chem.*, 1886, [ii], **33**, 290). The picrate melted at 215°, and as it separated from solution in peculiar, crystalline formations, which, under the microscope, resembled a highly divided palmatifid leaf, this compound may be used for the identification of the substance.

Since thioammeline results from the interaction of dicyanodiamide and thiocyanic acid, according to the equation

$$(CN\cdot NH_2)_2 + HSCN = HS\cdot C\lessgtr\begin{matrix}N:C(NH_2)\\N\cdot C(NH_2)\end{matrix}\gtrless N \quad . \quad . \quad (2)$$

it is not possible to suppress its formation, as dissociation of ammonium thiocyanate to a small extent cannot be avoided under the conditions of the experiment.

Residue *B* was pure thioammeline, generated as above from small quantities of dicyanodiamide and ammonium thiocyanate which had escaped change. This was proved by evaporating to dryness at 100° a solution of 2 grams of dicyanodiamide and 3·6 grams of ammonium thiocyanate in 50 c.c. of water, when 0·29 gram of thioammeline was obtained. For this reason, evaporation of the solution to dryness in the first instance was found to be the most efficient method for preparing a pure product, and the addition of about a gram of ammonium thiocyanate to the fusion when the reaction has been in progress for two hours is advisable. When an excess of the salt was used at the outset of the experiment, the yield of thioammeline was increased.

Should the crystals of guanidine thiocyanate show opalescence after crystallisation from, and while still in, the mother liquor, a second solution and filtration is necessary to remove the last traces of thioammeline. On account of the great solubility of guanidine thiocyanate in water, its complete separation in crystalline form is tedious; it may be recovered as carbonate by mixing the viscous mother liquor with about four volumes of alcohol, and, after the addition of the requisite amount of potassium hydroxide, the guanidine is precipitated by a current of carbon dioxide.

Apart from its practical value, the reaction is of theoretical interest, since it is obvious that depolymerisation of dicyanodiamide

must be the first phase of the change in order to yield guanidine in such quantity as required by equation (1), whilst the formation of thioammeline, the constitution of which has been clearly demonstrated by Klason (*loc. cit.*), according to equation (2), would be difficult to explain on the basis of the "cyanoguanidine" structure of dicyanodiamide.

Considering that Bamberger and Dieckmann (*loc. cit.*) obtained diguanide by heating guanidine hydrochloride at 185°, there can be no doubt that the latter was first formed in their preparation of diguanide from dicyanodiamide. This has been verified from qualitative experiments, which, however, were of no practical interest; on the other hand, very encouraging results have been obtained in the preparation of methyl- and ethyl-guanidine, an account of which is reserved for a future communication.

So far as the authors are aware, none of the methods hitherto described for the preparation of guanidine can compare with the process now set forth, either in respect of cost, simplicity, or yield of pure product. In this connexion, it may be useful to recount the authors' experience of Ulpiani's method (1909, D.R.-P. 209431) for the preparation of guanidine nitrate by the action of aqua regia at 60—65° on dicyanodiamide. A quantitative yield is claimed. Since the change (indirect oxidation) is accompanied by the evolution of much carbon dioxide and nitrogen from dicyanodiamidine simultaneously produced, the maximum yield of guanidine is represented by the ratio $C_2H_4N_4 \longrightarrow CH_5N_3,HNO_3$; from three carefully conducted experiments, the best yield was 26 grams of guanidine nitrate from 42 grams of pure dicyanodiamide, equal to 42·7 per cent. of the theoretical calculated on the foregoing ratio. It is evident from this result that not less than two molecules of dicyanodiamide are involved in the production of one of guanidine by this method.

The assay of dicyanodiamide was conveniently conducted by hydrolysis, as follows: 2 grams of the powdered sample were mixed with 25 c.c. of water, *N*-hydrochloric acid was added until the alkaline impurities were neutralised, using methyl-orange as indicator, after which the product was heated for forty-five minutes at 100° with 25 c.c. of *N*-acid. The residual acidity was determined by titration with *N*-sodium hydroxide. Each c.c. of *N*-acid neutralised is equal to 0·084 gram of dicyanodiamide.

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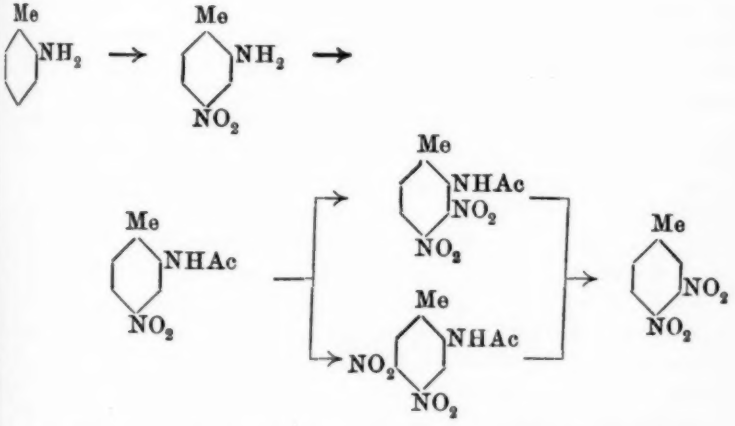
CXXVIII.—*The Synthesis of some Nitro-derivatives of Toluene.*

By Oscar Lisle Brady and Percy Noel Williams.

In the course of an investigation it was found necessary to prepare a considerable quantity of pure 3:4-dinitrotoluene. This compound is formed with the 2:3- and 2:5-isomerides by the nitration of *m*-nitrotoluene, and can be readily separated from the mixture by freezing (Beilstein and Kuhlberg, *Annalen*, 1870, **155**, 25; Haeussermann and Grell, *Ber.*, 1894, **27**, 2209; Holleman and Sirks, *Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 280). This method is satisfactory, although the yields are not large. Haeussermann and Grell (*loc. cit.*) mention the preparation from 3-nitro-*p*-toluidine by the Sandmeyer reaction, but do not give details. As a trial of Haeussermann and Grell's method did not give good results, and as *m*-nitrotoluene was unobtainable at the time and its preparation on a laboratory scale was very tedious, other methods of preparation of 3:4-dinitrotoluene were considered. The present paper deals with one of these methods. The starting material was *o*-toluidine, and the reactions involved may be summarised as follows:



The nitration of *o*-toluidine to 4-nitro-*o*-toluidine has been described by Noelting and Collin (*Ber.*, 1884, **17**, 265), but by a modification of their process, the separation of the isomeric nitrotoluidines formed has been greatly simplified. The yields obtained to the stage of the dinitrotoluidines were satisfactory, but the

removal of the amino-group from these compounds did not prove as easy as experience with similar compounds had led the authors to expect, and the yield of 3:4-dinitrotoluene was disappointing. On the other hand, the oxidation of the amino-group in the dinitrotoluidines to the nitro-group by means of Caro's acid proceeds very smoothly and provides a convenient method of synthesis of 2:3:4- and 2:4:5-trinitrotoluenes, which hitherto have been obtained only by the nitration of *m*-nitrotoluene and separation of the two isomerides by fractional crystallisation (Hepp, *Annalen*, 1882, **215**, 366) or by nitration of the rare 2:3- and 2:5-dinitrotoluenes (Will, *Ber.*, 1914, **47**, 704).

Experimental.

4-Nitroaceto-o-toluidide.—One hundred grams of *o*-toluidine were dissolved in 1087 c.c. of sulphuric acid (D 1·8), care being taken to avoid rise of temperature. The mixture was cooled below 0° in a freezing mixture, and a mixture of 163 c.c. of sulphuric acid (D 1·8) and 50·8 c.c. of nitric acid (D 1·42) cooled to 0° slowly run in so that the temperature did not rise above 0°. When all the acid had been added, the mixture was allowed to remain for one hour. At this stage Noelting and Collin (*loc. cit.*) neutralised all the acid with sodium hydroxide. A more economical method which avoids a great increase in the bulk of the liquid and the formation of tarry products consists in adding to the nitration mixture one-half its bulk of water with thorough cooling and stirring. On keeping, the sulphate of 4-nitro-*o*-toluidine separated, and was removed by filtration and washed with alcohol. The yield of sulphate was about 60 per cent. of the theoretical. The 6-nitro-*o*-toluidine formed during the nitration (Green and Lawson, T., 1891, **59**, 1014, say 20 per cent.) remained in the filtrate. The sulphate was ground in a mortar with a slight excess of 10 per cent. sodium hydroxide, and the free base collected, washed thoroughly with water, dried, and acetylated with acetic anhydride.

Nitration of 4-Nitroaceto-o-toluidide.—A solution of 20 grams of 4-nitroaceto-*o*-toluidide in 60 c.c. of concentrated sulphuric acid was added slowly with stirring to 60 c.c. of nitric acid (D 1·5) cooled in ice. When all the solution had been added, the mixture was allowed to remain in ice for thirty minutes, and then poured into 4 litres of ice-water. The solid separating was collected at once and thoroughly washed by grinding three or four times in a mortar with water and filtering. A 70 to 80 per cent. yield of the mixed dinitroaceto-*o*-toluidides was obtained.

Separation of the Dinitro-o-toluidines.—Fifty grams of the mix-

ture of dinitroaceto-*o*-toluidides were hydrolysed by heating for four or five hours on the water-bath with a mixture of 200 c.c. of concentrated sulphuric acid and 400 c.c. of water. On cooling the mixture, filtering, and washing the precipitate, first with 50 per cent. sulphuric acid and then with water, a 45 per cent. yield of a substance melting at 122° was obtained. On diluting the filtrate, a 25 per cent. yield of a material melting at 150—170° was precipitated. The compound melting at 122° was recrystallised several times from alcohol until the product was of constant melting point, and oriented by conversion into 2:3:4-trinitrotoluene (see below). 3:4-Dinitro-*o*-toluidine crystallises in lustrous, yellowish-brown needles melting at 131—131·5° (Found: N = 21·5. $C_7H_7O_4N_3$ requires N = 21·3 per cent.).

The substance melting at 150—170° was recrystallised twice from alcohol and oriented by conversion into 2:4:5-trinitrotoluene (see below). 4:5-Dinitro-*o*-toluidine crystallises in yellow needles melting at 191—191·5° (Found: N = 21·6. $C_7H_7O_4N_3$ requires N = 21·3 per cent.).

Preparation of 3:4-*Dinitrotoluene.*—For this purpose it is not necessary to separate the mixture of dinitro-*o*-toluidines, as both give 3:4-dinitrotoluene on removal of the amino-group. Nine grams of the mixture were dried and dissolved in a mixture of 180 c.c. of freshly distilled absolute alcohol and 45 c.c. of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide). The solution was heated on the water-bath, and 27 grams of finely powdered dry sodium nitrite were added in small portions with vigorous shaking. When all the nitrite had been added, the mixture was heated for five minutes, cooled, and diluted with water. The oily solid which separated was crystallised first from hot nitric acid (D 1·4) to destroy tarry matter, and then from alcohol with the addition of animal charcoal, when pure 3:4-dinitrotoluene was obtained. The yield was not good, 2 grams only being obtained from 9 grams of the mixture of dinitrotoluidines.

Preparation of 2:4:5-*Trinitrotoluene.*—To Caro's acid, prepared from 10 grams of ammonium persulphate and 7 c.c. of concentrated sulphuric acid poured on 20 grams of crushed ice, a solution of 2 grams of 4:5-dinitro-*o*-toluidine (m. p. 191°) in 10 c.c. of 80 per cent. sulphuric acid was added. A clear solution was obtained which, on keeping overnight, deposited dinitronitrosotoluene; it was then diluted with water, and the precipitated nitroso-compound added to ten times its weight of nitric acid (D 1·5) and warmed until red fumes were no longer evolved. On cooling and diluting the solution, a crystalline precipitate of 2:4:5-trinitrotoluene was obtained which, after one recrystallisa-

tion from alcohol, was pure. The yield was about 80 per cent. of the theoretical.

Preparation of 2:3:4-*Trinitrotoluene.*—A solution of 3:4-dinitro-*o*-toluidine in 80 per cent. sulphuric acid was added to Caro's acid as above; in this case, however, the amine was precipitated by the dilution of the sulphuric acid, so the mixture was transferred to a stoppered bottle and left for four days, with frequent shaking. At the end of that time the precipitate was collected and treated with nitric acid, as in the previous case, when 2:3:4-trinitrotoluene was obtained in good yield.

The authors wish to express their thanks to the Director of Artillery for permission to publish this work.

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CXXIX—*Studies in Ring Formation. Part III. The Condensation of Aromatic Amines with α- and β-Diketones and with* 4:4′-*Diacetyldiphenyl.*

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The Condensation of Benzidine and Tolidine with Benzil and Glyoxal.

CONDENSATION products of benzidine and tolidine with benzil or glyoxal were described by Cain and Micklethwait (T., 1914, **105**, 1437), but the present authors, after carefully repeating their experiments, are unable to confirm the formulæ assigned by them to the products obtained from benzidine and these two diketones.

Whilst the condensation product from benzil and benzidine has now been obtained in a state of purity, its complete analysis and a determination of its molecular weight by the cryoscopic method have not led to any definite conclusions as to its structure. Condensation seems to take place in a more complex manner than is assumed by the above authors. Hydrolysis of the product with mineral acid showed that more molecules of benzil than of benzidine enter into the reaction. Again, although such a condensation might be expected to proceed quantitatively, we have not succeeded in obtaining more than 70 per cent. of the calculated

yield, nor is an appreciable quantity of acetylbenzidine formed, as might be supposed.

Of the products obtained from glyoxal, that formed with benzidine is a highly insoluble non-crystalline mass of unknown molecular complexity. The condensation of glyoxal and tolidine gave a substance of the empirical formula found by Cain and Micklethwait, but its insolubility renders a molecular-weight determination impossible, so that it may possibly be formed by the condensation, not of one molecule of glyoxal with one of tolidine, but by the condensation of two molecules of each together.

The Condensation of Amines and Diamines with Acetylacetone and Benzoylacetone.

Condensation products of acetylacetone and benzoylacetone with benzidine and other bases have previously been described by one of us (T., 1915, **107**, 1495; 1917, **111**, 1). Further examples have now been studied. Among other results, it has been found that *monoacetyl*iso*propylidenetolidine* is a liquid at the ordinary temperature, and *diacetyl*iso*propylidenetolidine* a solid melting at 108° (uncorr.), whereas the corresponding compounds from benzidine melt respectively at 137° and 198° (compare benzylidene-*o*-toluidine, a liquid, and benzylideneaniline, m. p. 48—49°).

Combes (*Bull. Soc. chim.*, 1888, [ii], **49**, 89), who first studied the action of amines on acetylacetone, stated that the product of condensation of *p*-toluidine and acetylacetone melted at 39—40°, apparently referring to the trimethylquinoline formed by its further condensation in the presence of sulphuric acid. Pfitzinger (*J. pr. Chem.*, 1888, [ii], **38**, 40) gives the melting point of the trimethylquinoline in question as 63—64°. The present authors have found that *p*-toluidine and acetylacetone condense under the influence of heat alone to give the trimethylquinoline, the melting point of which is 64°, a fact which renders *p*-toluidine an abnormal compound as regards its action on acetylacetone.

Ketones of the Diphenyl Series. Attempts to Condense 4:4′-Diacetyldiphenyl with o-Phenylenediamine.

Hitherto our knowledge of ketones derived from diphenyl has been restricted to phenylacetophenone, 4-phenylbenzophenone, 4:4′-dibenzoyldiphenyl, diphenylyl benzyl ketone, and diphenylyl α-naphthyl ketone. Satisfactory proof of the constitution of these ketones has only been given in the case of 4:4′-dibenzoyldiphenyl. This substance, originally obtained by Wolf (*Ber.*, 1881, **14**, 2031)

by the action of benzoyl chloride on diphenyl in the presence of aluminium chloride, was prepared by Ullmann (*Annalen*, 1904, **332**, 79) from 4-iodobenzophenone and copper bronze, and thus shown to be the 4:4′-derivative. From this it follows that Wolf's phenylbenzophenone is a 4-derivative.

Various errors have been noticed in the literature, traceable to the work of Adam (*Ann. Chim. Phys.*, 1886, [vi], **15**, 224). This author, as a result of a more or less systematic study of the Friedel and Crafts reaction in the diphenyl series, concluded that in all such reactions, save one, 3-substituted diphenyls were produced, a conclusion based on the fact that these compounds gave, on oxidation, an acid melting at 160—161°, which Adam took to be diphenyl-3-carboxylic acid. His one exception, diphenylbenzophenone, obtained from carbonyl chloride and diphenyl, proved to be identical with the product obtained by Weiler (*Ber.*, 1873, **6**, 1181) from methylal and diphenyl, and gave on oxidation an acid (diphenyl-4-carboxylic) melting at 217—218°.

Adam's phenylacetophenone was stated by Vorländer (*Ber.*, 1907, **40**, 4535) to be the 4-derivative, since derived compounds formed anisotropic liquids, a property which would not be possessed by 3-derivatives.

The action of acetyl chloride on diphenyl in the presence of aluminium chloride has now been shown to result in the formation of 4-phenylacetophenone (m. p. 121°) and 4:4′-*diacetyldiphenyl* (m. p. 190—191°). The former (identical with Adam's phenylacetophenone) gives, on oxidation, diphenyl-4-, and not, as stated by Adam, diphenyl-3-carboxylic acid. The constitution of these ketones has been set beyond doubt by their synthesis, respectively, from 4-cyano- and 4:4′-dicyano-diphenyl by means of magnesium methyl iodide.

Since Adam's phenylacetophenone is the 4-derivative, and since his supposed 3-ethyldiphenyl gave this ketone on partial oxidation, this ethyl derivative must be 4-ethyldiphenyl. It is evident, similarly, that his supposed 3-methyldiphenyl is actually 4-methyldiphenyl.

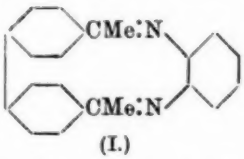
Again, the diphenylyl benzyl ketone obtained by Päpcke (*Ber.*, 1888, **21**, 1339) by the action of phenylacetyl chloride on diphenyl in the presence of aluminium chloride, has now been shown definitely to be the 4-derivative by its synthesis from 4-cyanodiphenyl and magnesium benzyl chloride.

In addition, 4:4′-*diphenyldiacetyldiphenyl*, which is not produced to any extent in the Friedel and Crafts reaction mentioned above, has been prepared from 4:4′-dicyanodiphenyl.

It is evident from the above that in all known Friedel and

Crafts' reactions between diphenyl and halogen compounds, 4-derivatives are obtained, a fact which justifies Schmidlin and Garcia-Banùs (*Ber.*, 1912, **45**, 3183) in their assumption as to the constitution of the diphenylyl *α*-naphthyl ketone prepared by them.

This investigation into the ketones of the diphenyl series was made as the result of desiring to determine the spatial relation of the two acetyl groups in 4:4′-diacetyldiphenyl; this ketone might be expected, if the Kaufler formula for derivatives of diphenyl is valid, to condense with *o*-phenylenediamine to give a compound of the constitution (I). When the two substances in



(I.)

question are warmed together in acetic acid solution, condensation occurs, and a yellow solid is precipitated from the mixture on adding methyl or ethyl alcohol. As in the case of the condensation product of benzil and benzidine, however, it has not been found possible to ascribe a definite constitution to the product obtained, although the evidence is probably in favour of a *compound* formed by the condensation of two molecules of ketone with one of diamine.

Experimental.

Condensation of Benzil with Benzidine.

This condensation has been carried out as described by Cain and Micklethwait (*loc. cit.*), 1·84 grams of benzidine, 2·1 grams of benzil, and 10 c.c. of glacial acetic acid being used. After twenty minutes' heating of this mixture on the boiling-water bath, it was cooled and scratched, when the canary-yellow precipitate separated, further warming then causing further separation of precipitate. The yield was found to be increased by periodic cooling and scratching. The precipitate was collected, washed with a little glacial acetic acid and then with dilute acetic acid, and dried in a vacuum over potassium hydroxide. The greenish-yellow solid so obtained (equivalent in quantity to a 70 per cent. conversion to the supposed compound) crystallised readily from benzene, but a less green product was obtained using xylene as solvent, the crystals being then washed with light petroleum [Found: C = 85·1; H = 5·5. C = 85·2; H = 5·7. N = 5·3, 5·3 per cent. M.W. (by cryoscopic method in bromoform) = 496].

The *substance* is readily soluble in hot xylene, benzene, or pyridine, and almost insoluble in cold xylene, benzene, alcohol, or glacial acetic acid.

An attempt to obtain Cain and Micklethwait's ethyl alcohol additive compound was made as follows: the condensation product was collected, dissolved in benzene, the solution evaporated to dryness after the addition of a little alcohol, and the residue again treated with alcohol and the latter evaporated. Evaporation of the benzene solution obtained as above, without adding alcohol, gave a well-defined product identical with that obtained in the presence of alcohol (Found: C = 85·0; H = 5·5; N = 5·7 per cent.).

The *substance* melted at 239—240°, a mixture with the product from xylene (above) melting at the same temperature.

Similarly, an attempt was made to prepare Cain and Micklethwait's methyl alcohol additive compound, following their described method as closely as possible. The product could not be melted under methyl alcohol even on prolonged boiling, and, when dried, melted at 231—234° (Found: C = 80·0; H = 4·2; N = 5·8 per cent.).

The product was again treated with methyl alcohol (for the fourth time), and the whole evaporated (Found: C = 80·4; H = 3·9 per cent.; m. p. 231—234°).

It was then crystallised from xylene (Found: C = 81·3; H = 4·9 per cent.; m. p. 233—236°), a second crystallisation from xylene giving a product melting at 234—237° (Found: C = 83·7; H = 5·0 per cent.).

The present authors attribute the low melting point, etc., of the first of these products to the fact that the green impurities were still present, and the subsequent results to the removal of those impurities.

In order, if possible, to throw more light on the condensation just described, the melting points of mixtures of benzil and benzidine have been determined. The benzil used was purified by recrystallisation from alcohol, and melted at 94·4°. The benzidine was purified by recrystallisation successively from water and dilute alcohol, and then several times from alcohol. Pure benzidine obtained in this way melts at 127·4°. All mixtures of benzil and benzidine melted below the latter temperature, the curve of mixed melting points being part of an inverted parabola, the axis of which ran vertically from the point representing two molecules of benzil to one of benzidine. No evidence for the formation of a compound was forthcoming.

Condensation of Benzidine with Glyoxal.

On effecting the condensation as described by Cain and Micklethwait, a dark brown, amorphous precipitate was obtained. On drying, it gave a hard mass, an examination of which gave no results worth recording.

Condensation of Tolidine with Glyoxal.

This condensation gave the results published by Cain and Micklethwait (Found: C=82·2; H=5·9; N=12·2. Calc. for $C_{16}H_{14}N_2$: C=82·0; H=6·0; N=12·0 per cent.). It was not found possible to carry out a determination of molecular weight, so that the constitution of the substance cannot be deduced.

Condensation of Acetylacetone with p-*Toluidine.*

A mixture of *p*-toluidine and acetylacetone in molecular proportions was gently boiled for an hour. On cooling, the whole set solid, a small portion, after being left in contact with porous porcelain, melting at 64°, and at the same temperature after crystallisation from light petroleum. Almost the theoretically possible yield of 2:4:6-trimethylquinoline was thus obtained (Found: N=8·2. Calc.: N=8·2 per cent.).

Monoacetylisopropylidenetolidine and its p-*Nitrobenzylidene Derivative,* $NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_3Me{\cdot}C_6H_3Me{\cdot}N{:}CMe{\cdot}CH_2Ac$.

A boiling solution of 2·1 grams of tolidine in 15 c.c. of xylene was slowly treated with 1 gram of acetylacetone dissolved in 5 c.c. of xylene, heating being continued for a further hour. On distilling off the xylene, a dark, viscid liquid was obtained, which could not be caused to crystallise. In order to confirm its constitution, it was converted into the *p*-nitrobenzylidene derivative by boiling it in alcoholic solution with a slight excess of *p*-nitrobenzaldehyde. The brick-red precipitate obtained in this way was crystallised from a mixture of pyridine and alcohol (Found: N=10·5. $C_{26}H_{25}O_3N_3$ requires N=9·8 per cent.).

The high percentage of nitrogen found was due to the presence of a small quantity of di(*p*-nitrobenzylidene)-tolidine, which, when working with barely sufficient material, cannot readily be removed.

N-p-*Nitrobenzylidenemonoacetylisopropylidenetolidine* melts at 245—247°, is readily soluble in hot pyridine, and sparingly so in cold alcohol or acetone.

*Diacetyl*isopropylidenetolidine, $(\cdot C_6H_3Me\cdot N{:}CMe\cdot CH_2Ac)_2$.

A solution of tolidine (8 grams) in 15 grams of acetylacetone was heated at the boiling point for three hours, the excess of diketone distilled off, and the yellow, crystalline residue obtained on cooling crystallised from a mixture of xylene and light petroleum, from which it separated in yellow needles melting at 108° (uncorr.) (Found: N = 7·7. $C_{24}H_{28}O_2N_2$ requires N = 7·4 per cent.).

2:4:8:2′:4′:8′-*Hexamethyl*-6:6′-*diquinolyl*.

The preceding compound was heated with ten times its weight of concentrated sulphuric acid at 125° for two hours, the cooled solution poured into water, the resulting solution rendered alkaline, and the white precipitate collected and crystallised from xylene (Found: N = 8·4. $C_{24}H_{24}N_2$ requires N = 8·2 per cent.).

The *base* crystallises from xylene in minute cubes melting at 252·5°, and is almost insoluble in either hot or cold alcohol, carbon tetrachloride, or toluene.

The *platinichloride* was obtained in the usual manner, and forms brownish-yellow needles (Found: Pt = 26·2. $C_{24}H_{24}N_2,H_2PtCl_6$ requires Pt = 26·14 per cent.).

*Monobenzoyl*isopropylidenebenzidine,
$NH_2\cdot C_6H_4\cdot C_6H_4\cdot N{:}CMe\cdot CH_2Bz$.

A solution of 3·24 grams of benzoylacetone in 15 c.c. of xylene was added gradually to a boiling solution of 3·68 grams of benzidine in 15 c.c. of xylene, the heating continued for a further hour, the solvent removed by distillation, and the yellow residue crystallised from a mixture of pyridine and alcohol, when it separated in slender, pale yellow needles melting at 179° (Found: N = 8·7. $C_{22}H_{20}ON_2$ requires N = 8·5 per cent.).

*Acetyl*isopropylidenebenzoylisopropylidenebenzidine,
$CH_2Ac\cdot CMe{:}N\cdot C_6H_4\cdot C_6H_4\cdot N{:}CMe\cdot CH_2Bz$.

A boiling solution of the preceding compound (0·761 gram) in 10 c.c. of xylene was slowly treated with a solution of 0·232 gram of acetylacetone in 5 c.c. of xylene, and the reaction allowed to complete itself during a further short boiling. On removing the xylene by distillation, a yellow residue remained, which was crystallised from a mixture of pyridine and alcohol (Found: N = 7·0. $C_{27}H_{26}O_2N_2$ requires N = 6·8 per cent.).

The compound forms yellow leaflets melting at 234—236°, and is sparingly soluble in alcohol, readily so in cold chloroform, and dissolves in hot pyridine.

Monobenzoylisopropylidenetolidine,
$NH_2 \cdot C_6H_3Me \cdot C_6H_3Me \cdot N{:}CMe \cdot CH_2Bz$.

This substance was obtained in a manner similar to that described for the corresponding benzidine compound, and crystallises from a mixture of pyridine and alcohol in pale yellow needles melting at 170°. It acquires a green colour in moist air, owing to partial oxidation (Found: N = 8·0. $C_{24}H_{24}ON_2$ requires N = 7·9 per cent.).

Condensation of Acetyl Chloride with Diphenyl.

(a) *Preparation of 4-Phenylacetophenone.*—Acetyl chloride (8 grams) was mixed with 100 c.c. of carbon disulphide and a large excess of diphenyl (35 grams), and 20 grams of anhydrous aluminium chloride were slowly added. The reaction was carried to completion by heating, and the cooled mixture decomposed with ice and dilute hydrochloric acid. The carbon disulphide was removed in a current of steam, and the residue cooled, filtered, and dried. The white solid so obtained was extracted with boiling light petroleum until a sample of the residue, on drying, melted at 115—120°. The residue, consisting of almost pure phenylacetophenone, was crystallised from alcohol, and melted at 120—121° (uncorr.). It possessed the properties ascribed to it by Adam (*loc. cit.*) (Found: C = 85·2; H = 6·2. Calc.: C = 85·7; H = 6·1 per cent.).

(b) *Preparation of Phenylacetophenone and 4:4′-Diacetyldiphenyl.*—Anhydrous aluminium chloride (26·7 grams) was covered with a mixture of 100 c.c. of carbon disulphide and 15·4 grams of diphenyl. Acetyl chloride (15·7 grams) was then slowly added, and the evolution of hydrogen chloride allowed to become complete by subsequent heating in warm water. The carbon disulphide was evaporated, the mixture decomposed as before, and the resulting white solid collected and dried. Elaborate fractional crystallisation from alcohol gave phenylacetophenone (moderately soluble) and *4:4′-diacetyldiphenyl* (sparingly soluble). The latter was purified by crystallisation successively from dilute acetic acid, alcohol, and carbon tetrachloride; it forms almost colourless leaflets melting at 190—191° (uncorr.) (Found: C = 80·5; H = 5·9. $C_{16}H_{14}O_2$ requires C = 80·7; H = 5·9 per cent.).

Preparation of 4-Cyanodiphenyl.

The preparation of this substance from diazotised 4-aminodiphenyl and potassium cuprocyanide proved unsatisfactory, a large quantity of a polymeride being formed. It is interesting to note that Kaiser (*Annalen*, 1890, **257**, 100) obtained a moderately good yield of diphenyl-5-carboxylic acid by the hydrolysis of the total crude product. The method described by Rassow (*Annalen*, 1894, **282**, 143) for the preparation of the nitrile was finally adopted; it is, however, tedious, and gives a large quantity of the polymeride.

Preparation of 4-Phenylacetophenone (4-Acetyldiphenyl).

A solution of 0·3 gram of 4-cyanodiphenyl in 100 c.c. of benzene was added to a Grignard reagent prepared from 1·5 gram of methyl iodide, 0·24 gram of magnesium, and 40 c.c. of ether. The ether was then removed by distillation, and the residue heated to boiling for four hours, then cooled, decomposed with water and acid, and the benzene layer separated, dried, and evaporated. The residue was extracted with boiling alcohol in the presence of wood charcoal, the extracts filtered, evaporated, and the residue treated as before. In this way, a small quantity of a white solid was obtained, crystallising from alcohol in colourless needles melting at 120—121°, and producing no depression of the melting point of the phenylacetophenone prepared as described above. The latter is therefore 4-phenylacetophenone.

Oxidation under the exact conditions described by Adam (*loc. cit.*) gave a mixture of unchanged ketone and diphenyl-4-carboxylic acid melting at 220°. The latter was extracted from the mixture by means of sodium hydroxide, and the extract filtered and acidified, etc. The low melting point (160—161°) found by Adam was evidently due to the presence of unchanged ketone.

Preparation of 4-Diphenylyl Benzyl Ketone.

(*a*) This substance was obtained by condensing diphenyl (1 mol.) with phenylacetyl chloride (2 mols.) in carbon disulphide solution by means of aluminium chloride, the reaction mixture being treated in the usual manner. The black, tarry solid obtained in this way was extracted repeatedly with boiling alcohol, the extracts precipitated with water, and the resulting yellow solid freed from phenylacetic acid by extraction with hot aqueous ammonia. The product was finally crystallised repeatedly from

alcohol, and then melted at 150°. Its properties agreed with those described by Päpcke (*loc. cit.*).

(*b*) A solution of 0·9 gram of 4-cyanodiphenyl in 100 c.c. of benzene was added to a Grignard reagent prepared from 2 grams of benzyl chloride, 0·36 gram of magnesium, and 50 c.c. of ether. The latter solvent was removed by distillation, the residue heated to boiling for six hours, and then decomposed in the usual manner. Extraction of the solid finally obtained with light petroleum and benzene gave a white solid melting, after crystallisation from alcohol, at 150°, and producing no depression of the melting point of the product from (*a*). The latter is therefore 4-diphenylyl benzyl ketone.

Preparation of 4:4′-*Dicyanodiphenyl.*

This substance has hitherto only been prepared from the corresponding disulphonic acid by fusion with potassium cyanide. The following method was found to be more convenient.

A solution of 17·2 grams of benzidine in 42·5 c.c. of concentrated hydrochloric acid and 150 c.c. of water was diazotised with a concentrated solution of sodium nitrite, and the solution added gradually to a warm solution prepared by mixing 50 grams of cupric sulphate pentahydrate (in 200 c.c. of water) with 55 grams of potassium cyanide (in 100 c.c. of water), benzene being added to prevent the accumulation of froth. The reaction was completed by heating to a hot water-bath temperature, the brown precipitate collected, washed with boiling water, and dried, and then extracted repeatedly with much boiling alcohol; the filtered extracts were precipitated with water, and the combined precipitates dried and crystallised from pyridine. The pure nitrile obtained in this way melts at 235° (uncorr.), as stated by Doebner (*Ber.*, 1876, **9**, 272).

4:4′-*Diacetyldiphenyl.*

A solution of 2 grams of 4:4′-dicyanodiphenyl in 150 c.c. of benzene was added to a Grignard reagent prepared from 6 grams of methyl iodide, 1 gram of magnesium, and 50 c.c. of ether. The ether was removed by distillation and the residue heated to boiling for six hours, then treated with water and excess of dilute sulphuric acid, and the mixture again heated for an hour, it being thought possible that, owing to the extreme difficulty of hydrolysing the dinitrile (see Doebner, *Annalen*, 1874, **172**, 116), the intermediate magnesium additive compound formed in the present reaction would only slowly be decomposed by cold acid (see Forster

and Judd, T., 1905, **87**, 368). The benzene layer was finally separated and dried. When evaporated slightly, it deposited the diacetyldiphenyl in clusters of needles or leaflets melting at 190°, and producing no depression of the melting point of the diacetyldiphenyl prepared from diphenyl and acetyl chloride (above). The latter is therefore the 4:4′-derivative.

4:4′-Diphenyldiacetyldiphenyl.

A solution of 2 grams of 4:4′-dicyanodiphenyl in 200 c.c. of benzene was added to a Grignard reagent prepared from 7 grams of benzyl chloride, 1 gram of magnesium, and 60 c.c. of ether, when a reddish-brown precipitate was formed. The ether was removed by distillation, the residue heated to boiling for four hours, decomposed with water and dilute acid, again heated, and finally filtered, and the two layers were separated. The residue from the filtration was combined with the residue obtained by evaporating the benzene solution, dried, and crystallised from pyridine, when it formed white leaflets melting at 224° (uncorr.) (Found: C=86·7; H=5·6. $C_{28}H_{22}O_2$ requires C=86·2; H=5·6 per cent.).

Both of the ketones just described react normally with phenylhydrazine.

Condensation of 4:4′-Diacetyldiphenyl with o-Phenylenediamine.

When the ketone and the diamine are gently heated together for a few minutes, a red colour is developed, owing to the formation of a *substance*, which is precipitated by alcohol and is insoluble in the latter. Condensation in slightly diluted glacial acetic acid (to preclude the formation, so far as possible, of benziminazole) gave, when equimolecular quantities of the reacting substances were taken, an orange-yellow product, obtained by precipitation of the acetic acid solution with methyl alcohol. On dissolving it in pyridine and precipitating with light petroleum, it was obtained in a microcrystalline condition (m. p. [indefinite] about 150°) (Found: C=84·7; H=5·7; N=4·2. $C_{38}H_{32}O_2N_2$ [2 mols. of ketone condensing with 1 mol. of base, with elimination of 2 mols. of water] requires C=83·2; H=5·8; N=5·1; $C_{22}H_{18}N_2$ [1 mol. of ketone, 1 mol. of base, elimination of 2 mols. of water] requires C=85·2; H=5·8; N=9·0 per cent.).

The small quantity of the product rendered a thorough investigation impossible, but it is thought that the evidence indicates the formation of a compound of the iminazole type by the condensa-

tion of two molecules of the diketone with one of *o*-phenylenediamine.

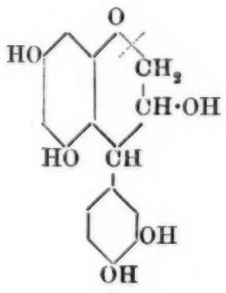
We desire to thank Mr. R. G. Hook for some help with one of the experiments, and the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this investigation.

THE UNIVERSITY CHEMICAL LABORATORIES,
SYDNEY, N.S.W. [*Received, August 30th*, 1920.]

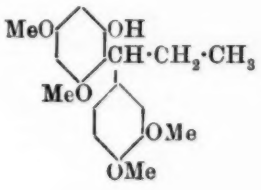
CXXX.—*The Constitution of Catechin. Part II.*

By MAXIMILIAN NIERENSTEIN.

In the previous communication (this vol., p. 971), provisional formulæ were suggested for catechin (I) and for the methylated reduction product (III) obtained by Kostanecki and Lampe (*Ber.*, 1907, **40**, 720) from catechin tetramethyl ether. At the same time, it was shown that Kostanecki and Lampe's substance may be oxidised to 3:4:2′:4′:6′-pentamethoxydiphenylacetic acid (IV).



(I.)



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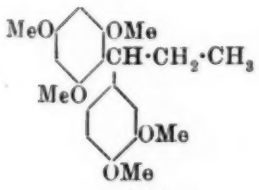

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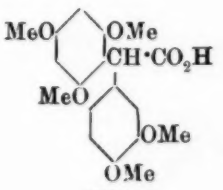
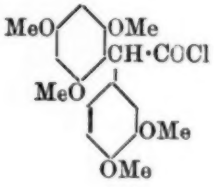


(IV.)

The present communication describes the synthesis of 3:4:2′:4′:6′-*pentamethoxy-αα-diphenylpropane* (III), which was

found to be identical in every respect with the methylated reduction product of Kostanecki and Lampe. The synthesis was carried out according to the following scheme: 3:4:2′:4′:6′-*pentamethoxydiphenylacetyl chloride* (V), on treatment with diazomethane (compare Clibbens and Nierenstein, T., 1915, **107**, 1491), yielded 3:4:2′:4′:6′-*pentamethoxydiphenylmethyl chloromethyl ketone* (VI), which, on reduction with metallic sodium and alcohol, gave 3:4:2′:4′:6′-pentamethoxy-αα-diphenylpropane (III).



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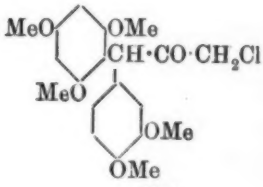
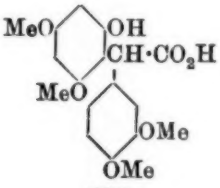
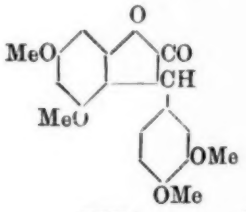


(VI.)

The intermediate *2′-hydroxy*-3 : 4 : 4′ : 6′-*tetramethoxy-αα-diphenylpropane* (II) has previously not been investigated; thus, Kostanecki and Lampe (*loc. cit.*) only refer to it as an oil, without further mention. It has now been obtained as a crystalline substance, which yields on oxidation *2′-hydroxy*-3:4:4′:6′-*tetramethoxydiphenylacetic acid* (VII). The latter substance behaves normally towards methyl sulphate, diazomethane, and acetyl chloride and pyridine, yielding the corresponding derivatives. On digestion with acetic anhydride and anhydrous sodium acetate, however, 3:5:3′:4′-*tetramethoxy-2-phenylcoumaran-1-one** (VIII) is formed, which is also produced when 3:4:2′:4′:6′-pentamethoxydiphenylacetic acid (IV) is treated with acetyl chloride according to Stoermer and Friderici's method (*Ber.*, 1908, **41**, 340).



(VII.)



(VIII.)

* The numbering of the coumaran nucleus is as suggested by Stoermer (*Annalen*, 1900, **312**, 258).

Experimental.

3:4:2′:4′:6′-*Pentamethoxydiphenylacetyl Chloride* (V).

Six and a-half grams of 3:4:2′:4′:6′-pentamethoxydiphenylacetic acid are heated on a water-bath for three hours with 10 grams of thionyl chloride. As much as possible of the unchanged thionyl chloride is distilled off under diminished pressure and the residue dissolved in dry benzene. The solid obtained by evaporating the benzene is left over solid potassium hydroxide in a vacuum for some time, so as to remove the adhering traces of thionyl chloride. The product crystallises from benzene in small clusters of prismatic needles, which melt at 76·5°. The yield is 98 per cent. of the theoretical (Found: Cl = 9·6. $C_{19}H_{21}O_6Cl$ requires Cl = 9·3 per cent.).

3:4:2′:4′:6′-*Pentamethoxydiphenylmethyl Chloromethyl Ketone* (VI).

To a solution of 6 grams of the acyl chloride in dry ether (according to Grignard), an ethereal solution of freshly prepared diazomethane from 30 c.c. of nitrosomethylurethane is added. When the evolution of nitrogen ceases, the same amount of diazomethane is again added, and the solution allowed to remain for several days, moisture being excluded. The ether, which contains an excess of diazomethane, is distilled off, and the residue crystallised from benzene. Large, glistening plates separate, which melt at 102° and have the characteristic odour of the chloromethyl ketones. The yield is 94 per cent. of the theoretical (Found*: C = 60·6; H = 5·9; Cl = 8·9. $C_{20}H_{23}O_6Cl$ requires C = 60·9; H = 5·8; Cl = 9·0 per cent.).

3:4:2′:4′:6′-*Pentamethoxy-aa-diphenylpropane* (III).

A solution of 6 grams of the ketone in about 200 c.c. alcohol is heated on a water-bath with 20 grams of metallic sodium until the latter disappears. The solution is subsequently reduced to about 50 c.c. and diluted with water. The precipitate crystallises from alcohol in small needles, which melt at 83—84°. This melting point is not depressed when mixed with the methylated reduction product of Kostanecki and Lampe (Found*: C = 69·2; H = 7·7. Calc.: C = 69·3; H = 7·5 per cent.).

* Dried over paraffin in a vacuum.

2′-Hydroxy-3:4:4′:6′-tetramethoxy-αα-diphenylpropane (II).

By distilling Kostanecki and Lampe's reduction product (deoxyhydrocatechin tetramethyl ether) under diminished pressure, the greater proportion is obtained as an oil boiling at 235—238°/10—11 mm. After remaining on ice for a short time, it readily solidifies. A few crystals of this substance are sufficient to cause the oil of other preparations to become semi-solid without previous distillation. Prepared by this method, any adhering oil may be removed by washing with light petroleum and subsequent drying on a porous plate. Three preparations from 10 grams of catechin tetramethyl ether gave 7·8, 6·2, and 8·1 grams, respectively, of the solid.* It crystallises from alcohol in rectangular plates, which feel oily and melt at 106°. The substance is soluble in the usual organic solvents, with the exception of light petroleum in the cold. The alcoholic solution turns violet with ferric chloride (Found†: C = 68·5; H = 7·4. $C_{19}H_{24}O_5$ requires C = 68·7; H = 7·2 per cent.).

On treatment with methyl sulphate, the theoretical yield of 3:4:2′:4′:6′-pentamethoxy-αα-diphenylpropane (III) is obtained. It melts at 83—84°, and this melting point is not depressed when mixed with the methylated reduction product of Kostanecki and Lampe.

2′-Hydroxy-3:4:4′:6′-tetramethoxydiphenylacetic Acid (VII).

Nine grams of 2′-hydroxy-3:4:4′:6′-tetramethoxy-αα-diphenylpropane suspended in 300 c.c. of a 20 per cent. solution of potassium hydroxide in water are oxidised on a boiling-water bath for four hours with 9 grams of potassium permanganate dissolved in 200 c.c. of water. The solution is filtered while hot, and, after cooling, acidified with dilute sulphuric acid. The dark-coloured precipitate is not filtered, but the solution extracted several times with ether, in which the precipitate dissolves. The ethereal extract, dried over anhydrous sodium sulphate, leaves a solid on evaporation, which, after several crystallisations from water,

* The reduction of catechin tetramethyl ether according to the method of Kostanecki and Lampe (*loc. cit.*) is apparently accompanied by some decomposition, since the crude reduction product has an odour of acetic acid. Several attempts were made to isolate some of the disintegration products by extracting the porous plate with alcohol. A small crop of needles was obtained from the alcoholic extract. They melted at 178—180°, which is the melting point given for veratric acid, but there was not enough material to establish their identity.

† Dried over paraffin in a vacuum

animal charcoal being used, yields long, prismatic needles melting at 168—169°, carbon dioxide being evolved. By prolonged drying over phosphoric oxide in a vacuum, or heating at 110°, one molecule of water is lost (Found*: $H_2O = 5{\cdot}0$. Calc.: $H_2O = 4{\cdot}9$ per cent.). The anhydrous product is powdery in appearance and melts at 172—173°, carbon dioxide being evolved. The substance is also soluble in alcohol or ethyl acetate, but insoluble in benzene or toluene. Both the aqueous and alcoholic solutions turn bluish-violet with ferric chloride. The yield is 78 per cent. of the theoretical (Found*: $C = 62{\cdot}2$; $H = 5{\cdot}9$. $C_{18}H_{20}O_7$ requires $C = 62{\cdot}1$; $H = 5{\cdot}7$ per cent.).

On methylation with methyl sulphate, 3:4:2′:4′:6′-pentamethoxydiphenylacetic acid (IV), melting at 150—151°, is formed. Diazomethane converts 2′-hydroxy-3:4:4′:6′-tetramethoxydiphenylacetic acid quantitatively into the corresponding methyl ester, which melts at 119°. Neither of these melting points is depressed when the compounds are mixed with the corresponding substances previously described (*loc. cit.*, p. 879).

The *acetyl* derivative is prepared by the action of acetyl chloride (3 grams) and pyridine (30 grams) on the anhydrous acid (3 grams). It crystallises from alcohol in prismatic needles, which melt at 183—184°, carbon dioxide being evolved (Found*: $C = 61{\cdot}5$; $H = 5{\cdot}7$. $C_{20}H_{22}O_8$ requires $C = 61{\cdot}5$; $H = 5{\cdot}6$ per cent.).

3:5:3′:4′-*Tetramethoxy*-2-*phenylcoumaran*-1-*one* (VIII).

One gram of 2′-hydroxy-3:4:4′:6′-tetramethoxydiphenylacetic acid is digested with 30 c.c. of acetic anhydride and 3 grams of anhydrous sodium acetate, and the mixture subsequently diluted with water. The precipitate obtained in this way crystallises from absolute alcohol in stout, prismatic needles, which melt at 117°. The yield is 85 per cent. of the theoretical (Found†: $C = 65{\cdot}4$; $H = 5{\cdot}5$. $C_{18}H_{18}O_6$ requires $C = 65{\cdot}5$; $H = 5{\cdot}4$ per cent.). The same product is also obtained when 3 grams of 3:4:2′:4′:6′-pentamethoxydiphenylacetic acid, dissolved in 20 c.c. of glacial acetic acid, are kept at the ordinary temperature for forty-eight hours with 50·4 c.c. of a solution of 100 c.c. glacial acetic acid and 2·12 grams of acetyl chloride (1 mol. of acetyl chloride). The greater part of the acetic acid is removed under diminished pressure and the residue precipitated with water. The product crystallises from absolute alcohol in stout, prismatic needles, which melt at 117°,

* Dried at 110°.

† Dried over paraffin in a vacuum.

and this melting point is not altered on mixing with the previous preparation. The yield is 91 per cent. of the theoretical.

The author is indebted to the Colston Society of the University of Bristol for a grant which has covered the expenses of this research.

BIOCHEMICAL LABORATORY,
CHEMICAL DEPARTMENT,
UNIVERSITY OF BRISTOL. [*Received, September 9th*, 1920.]

Note added October 1st, 1920.—Since this communication was submitted, a paper by Freudenberg (*Ber.*, 1920, **53**, [*B*], 1416) has appeared, in which he describes 3:4:2′:4′:6′-pentamethoxy-αγ-diphenylpropane as melting at 87—88°, which is the melting point given by the author (this vol., p. 972) for this substance. Freudenberg states, further, that Kostanecki and Lampe's methylated reduction product also melts at 87—88°, which is not correct. This substance melts at 83—84°, as given by Kostanecki and Lampe (*Ber.*, 1902, **40**, 720). The author has on five separate occasions prepared this product, and has always found it to melt at 83—84°. No difference of the melting point has been recorded by Ryan and Walsh (*Sci. Proc. Roy. Dublin Soc.*, 1916, **15**, 120), who have also prepared Kostanecki and Lampe's product. In view of Freudenberg's assumption that Kostanecki and Lampe's methylated reduction product is identical with 3:4:2′:4′:6′-pentamethoxy-αγ-diphenylpropane, the following mixed melting points were taken. They clearly disprove his contentions. (1) Kostanecki and Lampe's methylated reduction product (m. p. 83—84°) and 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αγ-diphenylpropane (m. p. 87—88°) giving a depression of 9 to 11 degrees. Similar results were obtained (August 11th, 1919) when three mixed melting points of these two substances were taken. (2) On the other hand, a mixture of Kostanecki and Lampe's product (m. p. 83—84°) with 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αα-diphenylpropane (m. p. 83—84°), described in the present communication, melted at 83—84° without the slightest depression, as already observed (April 26th, 1920), when two mixed melting points of these substances were taken.

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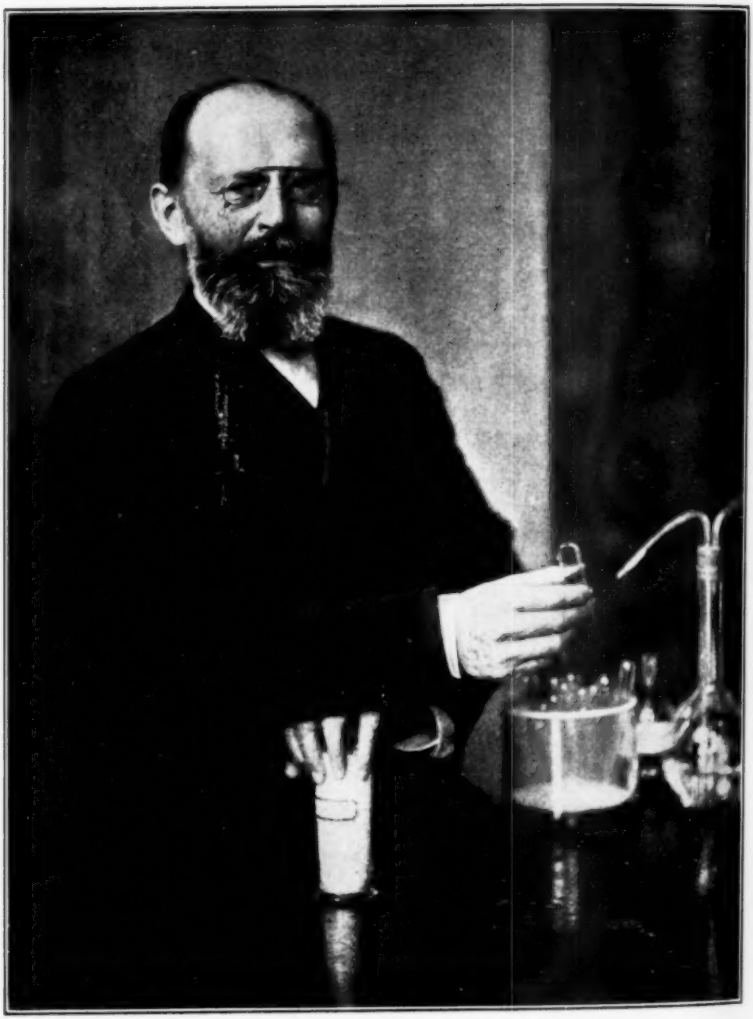

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EMIL FISCHER MEMORIAL LECTURE.

DELIVERED ON OCTOBER 28TH, 1920.

By MARTIN ONSLOW FORSTER, F.R.S., Treasurer.

To a world confused and lacerated by the bitter consequences of protracted warfare, at a time when every element of constructive and harmonising influence was most sorely needed, there came without premonition the announcement that Emil Fischer was dead. Inured as the nations had become to loss and disaster, it was probably with surprise that the scientific communities found the misfortune with which they were now confronted to be one in common with their former enemies. For the place which he occupied in our minds, first attained by his mastery of our subject, was hallowed by regard for his sterling disposition, compassion for his griefs, admiration for his outstanding power.

Emil Fischer was born on October 9th, 1852, at Euskirchen, some twenty-five miles from Cologne on the south-westerly high-road to the Eifel, about twenty miles from Bonn. Preceded by five sisters, he was the only son of Laurenz Fischer and Julie Poensgen. After leaving school at Bonn in 1869, he was apprenticed to his brother-in-law, Ernst Friedrichs, a timber merchant, but the occupation proving uncongenial, he became a pupil of Kekulé in 1871, and proceeded in the following year from Bonn to Strasbourg. Here he graduated in 1874 under von Baeyer, with whom he passed to Munich in 1875 as an assistant, becoming *Privatdozent*, and soon afterwards succeeding Volhard as *Ausserordentlicher Professor* in 1879. On the transference of Volhard to Halle, he was called to the chair of chemistry at Erlangen in 1882, whence he proceeded in 1885 to Würzburg in succession to the elder Wislicenus. He remained seven years at the Bavarian university, and on the demise of von Hofmann, in 1892, was appointed professor and director of the chemical institute in Berlin University, a post which he filled with increasing distinction until his death, which took place in the night of July 14th, 1919, at Wannsee, his country home. Such, in the barest outline, was Fischer's career—simple, straightforward, and honourable, like his nature.

Amongst those who came in contact with him, the impression left by Fischer is indelible, but the words to describe his personality

do not readily come. Physically commanding, his authority rested on the solid foundation of natural dignity unmarred by self-assertion. The brisk, upright carriage marked the man of action; the glowing eyes revealed his attitude of constant, keen inquiry; the impatience with trivialities was one aspect of his dominating, steadfast control of essentials. With ordinary human perception, it was impossible for anyone to escape his contagious enthusiasm, and yet all the time the master did not obscure the man; for although his daily demeanour was tinged with severity, his heart when revealed was deeply kind, and, in circumstances of relaxation, joyous. The alert presence, the ardent gaze, and the resonant voice will not fade from the recollection of those to whom they became the symbols of a treasured experience.

The salient quality of his life was unswerving singleness of purpose. Rapid satisfaction of reasonable professional ambition and the fact that he was only forty when summoned to Berlin did not distract him from his chosen path. The legitimate pride occasioned by the summons, the glad recognition of increased opportunities for research, the happy anticipation of entering an unlimited scientific environment were tempered by anxiety lest the social and ceremonial demands of the capital city should make serious inroads into the real work of his life. Even his sixtieth birthday celebration was, by his express desire, an almost domestic affair. Had he sought their presence, representatives of foreign academies, captains of industry, and councillors of State would gladly have joined his less exalted admirers in their tribute to the master, but the master himself ordained otherwise; with one exception, all the participants were former students, old colleagues, or members of his household.

Although the strictness with which Fischer confined his energy to affairs of chemistry was temperamental and due primarily to his natural and cultivated taste for the science, it is probable that his condition of health was a contributory factor. In the summer of 1881 he suffered an attack of mercury poisoning, consequent on studying the action between mercuric oxide and aliphatic hydrazines; neither he nor Bösler noticed until too late that mercury diethyl is produced, although the odour did not escape von Baeyer. The direct effects of this incident lasted three months, and ten years later Fischer fell a victim to the insidious onslaught of phenylhydrazine vapour. In his own words: "Dieses allerliebste Bäschen war meine erste und dauerndste chemische Liebe. Wir haben uns 15 Jahre lang ausgezeichnet miteinander vertragen, während viele andere Menschen gleich dadurch zu Schade kamen. Aber dann brach auch bei mir das [illegible]glück ein mit einer

chronischen und äusserst hartnäckigen Vergiftung, und es hat 12 Jahre gedauert, bis die Folgen beiseitigt waren."

It is characteristic of the man that his work is devoid of "popular" features, although common experience at every turn traverses the materials with which he dealt. The task of explaining the achievements of other great chemists, Pasteur, von Hofmann, or Sir William Perkin, for example, is relatively simple, but the fellow-citizen cannot hope to understand Fischer's chemistry of the breakfast-table until he has learned that the operations of digestion are essentially chemical transactions of a subtle nature. To the man whose sugar "melts" in tea, and who believes in a second member of the class, beet-sugar, and probably a third, namely, saccharin, how are the beauties of the sixteen stereoisomeric aldohexoses to be revealed? How is it possible to explain to a woman unversed in chemistry the family connexion between her silk dress and a scrambled egg?

In literary style his papers are uncompromisingly ascetic. The reader is quickly made aware of the subject about to be developed; in simple phrases the theme is pursued with a marked absence of verbal ornament, and the treatment, although complete, is so concise that a concluding summary of results is unnecessary. By this restraint Fischer has earned the gratitude of all chemists, for the labour of assimilating his enormous output has been reduced thereby to a minimum. Failing thorough discipline in writing abstracts of scientific memoirs, a study of the literary method adopted by Fischer offers the best possible training for the research chemist, old or young, in preparing reports of his own investigations.

By the time he had passed from Erlangen to Würzburg, Fischer's reputation had become magnetic, and from that period an increasing number of *doctorandi* sought admission to his laboratory. The aggregate of these must be several hundreds, including many nationalities, and with the passage of years he received, in addition to the customary distinctions accorded by his countrymen, the honours which it is the practice of foreign academies to offer. He became an Honorary and Foreign Member of the Chemical Society in 1892, a Foreign Member of the Royal Society in 1899, and an Honorary Member of the Royal Institution in 1904; he received the Davy Medal in 1890, the Nobel Prize for chemistry in 1902, and the Elliott Cresson Gold Medal from the Franklin Institute of Philadelphia in 1913.

Although too rarely seen in this country, he was warmly welcome when he came, and there is every ground for believing that the cordial feeling towards him which certainly existed

amongst British chemists was reciprocated, a concrete illustration of this being given by the fact that his eldest son, Hermann Fischer, passed two terms at Cambridge. Moreover, the many Englishmen who worked in his laboratory were quickly made aware of the kindly feeling towards them which he cherished, an experience adding appreciably to the benefit they derived from the association. Thus the veneration surrounding his name in this country could scarcely have been less, in depth and sincerity, than that acknowledged by his fellow-countrymen. It therefore gave lustre to the Perkin Jubilee in 1906 when, as President of the German Chemical Society, he conveyed the congratulations of that body to the veteran whilst conferring on him the Hofmann Medal.

The following year, in which he delivered the Faraday Lecture, marked another memorable occasion, postponed from 1895, when his condition of health did not permit acceptance of the invitation then given. The title of this address, namely, "Synthetical Chemistry in Relation to Biology," crystallises in a single phrase the profound significance of his own work; for, when reviewed as a chapter which is closed, this must be regarded as having established on a firm basis the fundamental, but bewildering, science of biochemistry. The assimilation of carbon dioxide and water by plants, the variety and complexity of saccharide molecules proceeding therefrom, the degradation of the proteins, the probable course of their synthesis from amino-acids, and the power of assemblage or of disruption exerted by enzymes on all these building materials of the animal and vegetable kingdoms, are subjects which Fischer not merely illuminated, but which he was the first to place in coherent arrangement and intelligible sequence. Recognition of the fact that all this was accomplished, not by revolutionary processes or tortuous theories, but by dexterous development of the thoughts and operations expanded by Liebig, von Hofmann, Pasteur, and von Baeyer, is perhaps the highest tribute which can be paid to his genius. Indeed, it offers the greatest inspiration to less gifted workers, who may thus be encouraged to perceive opportunities for discovery in adroit applications of classical principles: and pursuing methods of such simplicity may even arrive, by those devious paths which unfold themselves with delight and refreshment to an earnest inquirer, unexpectedly, as on the lifting of a curtain, directly at the threshold of a fundamental truth.

The natural curiosity which seeks to account for the biochemical trend of Emil Fischer's researches can only take refuge in predilection. There is nothing to explain it discoverable in family associations or in the tasks of his young manhood. Laurenz

Fischer, who passed the age of ninety-four, was an active and enterprising general merchant engaged in supplying the requirements of the peasant farmers inhabiting the Eifel; associated with his brothers, he was also concerned in a spinning mill and a brick-works close to his native town, and in the foundation of a brewery at Dortmund. Thus there existed every inducement for his only son to pursue a business career, and Ernst Friedrichs was quite positive in declaring his conviction that no good would come of Emil when the young apprentice relinquished an opportunity which appeared to him so full of promise. During this abortive attempt to transform him into a timber merchant, Fischer had been occupied with experiments in a home-made laboratory, and contemplated devoting himself to a study of physics; but his father, attracted by the handsome returns which the Rhenish chemical factories were already beginning to show, finally persuaded him to become a chemist.

His prepossession in favour of biochemistry was destined to resist another contrary influence. The doctorate thesis dealt with fluorescein and the phthalein of orcin, whilst his work on rosaniline in the Munich days would almost certainly have confirmed a less resolute mind in the pursuit of colour chemistry, then in the early flush of active growth. Moreover, this direction would have been a natural sequence to the powerful influence of von Baeyer, at that time immersed in the problems of indigotin synthesis. Indeed, it is a noticeable feature in the development of his character that Fischer's work detached itself so completely from household authority and so rapidly from early chemical environment. The only conspicuous mark of the training which he owed to von Baeyer was manipulative skill of the very highest order; this was revealed by results achieved with uninviting materials, frequently used in very small quantities, by the inception and adaptation of ingenious experimental devices, and by the rarity of occasion to revise earlier conclusions of his own. Fortunate he undeniably was, but the good fortune was thoroughly well earned by ceaseless industry. He was fortunate, for example, in the fact that nothing resembling the Walden inversion, that *bête noire* of optical activity, disturbed the aldohexose configuration. Imagine the confusion which would have arisen if gluconic and mannonic acids, instead of being smoothly interconvertible when heated with quinoline, had given mixtures of idonic, gulonic, galactonic, talonic, altronic, and allonic acids. Phenylhydrazine was a tremendous *coup*; but the preparation was according to plan, although its remarkable properties were fortuitous, a happy illustration of "to him that hath shall be given."

Nevertheless, that mysterious counterpoise of destiny, from which the greatest and the humblest cannot escape, plunged him into profound sorrow at the meridian of his career. In 1888 he had married Agnes Gerlach, but the happy union was cut short by her death in 1895. Thereafter his three boys were tended by Frln. Margarete Barth, who administered his household for the remaining twenty-four years of his life with watchful solicitude.

Early Work.

Fischer entered the field of organic chemical research at the opening of its brightest epoch. Largely in consequence of Kekulé's theory of benzene structure, the ground was ready for systematic cultivation: the advent of peace encouraged a willing and increasing band of workers to prepare themselves for fruitful labour; together they stood at the threshold of the imposing structure which was destined to arise during the next forty years.

The act of reading, in 1920, the paper on phenylhydrazine communicated from the Strasbourg laboratory in 1875, engenders the sensation of contemplating the modest source of a mighty river. In 1871, Strecker (with Römer) had treated benzenediazonium nitrate with excess of hydrogen potassium sulphite, obtaining a salt, which he represented by the formula

$$C_6H_5\cdot NH(:NH)\cdot SO_3K,H_2O,$$

and giving to diazotised aniline the expression since associated with his name. In 1875 Fischer showed that two salts arise from the diazotised base and neutral potassium sulphite, namely,

$C_6H_5\cdot N_2\cdot SO_3K$	and	$C_6H_5\cdot N_2H_2\cdot SO_3K + H_2O$
Potassium benzenediazonium sulphite.		Potassium phenylhydrazinosulphonate.

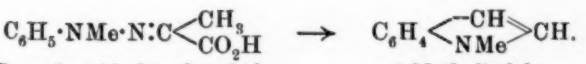
The latter was identical with Strecker's, and Fischer carried the inquiry to another stage by acting on it with benzoyl chloride, producing a substance (dibenzoylphenylhydrazine) which gave benzoic acid and phenylhydrazine hydrochloride when heated with hydrochloric acid; in this manner, phenylhydrazine itself was first obtained as an oil, which ultimately became solid. Later in the same year he simplified the preparation of the base by adding excess of sodium sulphite to benzenediazonium chloride, completing the reduction by means of zinc dust and hydrolysing the phenylhydrazinosulphonate with hot hydrochloric acid. Extending the process to diazotised sulphanilic acid, he prepared phenylhydrazinesulphonic acid, which had been actually obtained by Strecker and Römer (1871), because in this case they had heated the initial product with hydrochloric acid to remove excess of alkali sulphite.

Owing to the readiness with which hydrogen replaces the nitroso-group in secondary nitrosoamines, attempts by other chemists to prepare aliphatic hydrazines had failed. Fischer succeeded in reducing nitrosodimethylamine to dimethylhydrazine, and, having prepared diethylhydrazine and phenylethylhydrazine, he represented the primary hydrazine derivative by the formula

$$C_6H_5{\cdot}NH{\cdot}NH_2.$$

At the beginning of 1876 he described ethylhydrazine, which arose from hydrolysing diethylsemicarbazide, and expressed the intention of applying this process to the production of hydrazine itself. Throughout this and the succeeding year the simpler changes undergone by phenylhydrazine were studied, and it is noteworthy that at this period Fischer preferred the Kekulé formula for diazonium salts; he had regenerated potassium phenylhydrazinosulphonate from phenylhydrazine and potassium pyrosulphate, and, converting it by oxidation into the diazonium sulphite, was so impressed by the close experimental relationship between the two substances as to consider this an obstacle to the Strecker formula.

A survey of these early papers indicates the curious fact that although the power of phenylhydrazine to combine with aldehydes was quickly observed by Fischer, he does not appear to have recognised its tremendous value as a general agent for the carbonyl group until nearly ten years after discovering the base. This is probably due to the distraction offered by rosaniline (see below) and minor investigations, by his translation from Munich to Erlangen, and by the work on caffeine (1881), which was destined to lead him to the classification of purine derivatives. It is true that the action of acetaldehyde, benzaldehyde, and furfural had been noted, but it was probably the formation of the sparingly soluble and beautifully crystalline phenylhydrazone of pyruvic acid (1883) which revived the interest in his original discovery. The outstanding feature of 1884, an extraordinarily fruitful year, is the application of phenylhydrazine to carbonyl compounds in general, and the sugar group in particular. In that year, also, he explained the first transformation of a phenylhydrazone into an indole,



Pyruvic acid phenylmethylhydrazone. 1-Methylindole.

induced by the action of hydrochloric acid, and he re-assembled the evidence supporting his constitutional formula for phenylhydrazine, Erlenmeyer having advocated the alternative expression $C_6H_5{\cdot}NH_2{:}NH$.

Another interesting point in the early history of the phenylhydrazones is that the name for these important products of condensation does not appear to have been introduced by Fischer until 1888, when he represented them by the general expression $>C{:}N{\cdot}NHR$ instead of $>C<\begin{matrix}NH\\|\\NR\end{matrix}$; although many attempts, some of which are quite recent, have been made to resuscitate the cycloid representation, Fischer did not take part in the discussions, and the balance of evidence in favour of his formula preponderates.

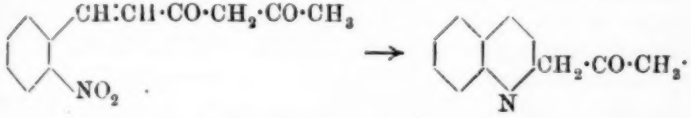
Even forty years ago, when the boundaries of organic chemistry were comparatively limited, the discovery of an entirely new class of highly reactive compounds by a novice must have been recognised as a portent; but the hydrazines were not the only subject with which Fischer's name came to be associated in the text-books with respect to work accomplished before he was twenty-five years of age. While in Munich he began collaboration with Otto Fischer, and in 1876 the cousins published their first joint paper on the rosaniline bases, obtaining from diazotised leucaniline the hydrocarbon, $C_{20}H_{18}$, melting at 58°. These experiments were made with the commercial product, and, on repeating them with the dye prepared from purified *p*-toluidine and aniline, they showed in 1878 that the corresponding leuco-base gives triphenylmethane, $C_{19}H_{16}$, melting at 93°, as recorded by Kekulé, Franchimont, and Hemilian. In view of its production from *p*-toluidine, the dye was named, somewhat unfortunately, "pararosaniline," and they proceeded to regenerate it from triphenylmethane by reducing Hemilian's trinitro-derivative and oxidising the paraleucaniline thus obtained. They concluded (1) that the rosanilines producible from aniline and the toluidines are homologues, of which the simplest, pararosaniline, has the composition $C_{19}H_{17}N_3$, whilst commercial fuchsine is a mixture, of which the principal constituent has the formula $C_{20}H_{19}N_3$, assigned by Hofmann, and (2) that the parent hydrocarbon of the whole group is triphenylmethane, of which, or of its homologues, the various leucanilines are triamino-derivatives.

Before proceeding to review the special branches with which Fischer's name is most conspicuously linked, it will be convenient here to notice a few developments of his earlier experiments which are not appropriately included in the following sections. For example, the conversion of suitable phenylhydrazones into derivatives of indole was extended in 1886, when it was found that anhydrous zinc chloride so greatly facilitates the removal of ammonia that the condensation products of primary and secondary arylhydrazines with all saturated ketones or ketonic acids con-

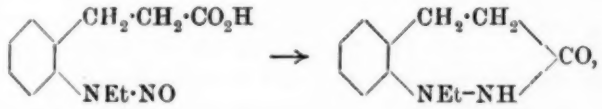
taining the methyl or methylene group adjacent to carbonyl can be transformed into the corresponding indole derivatives by loss of ammonia; as an illustration, acetonephenylhydrazone gives 2-methylindole,

A similar change proceeds with phenylhydrazones of aldehydes containing the methylene group next to the aldo-nucleus, and dimethylindole, methylethyl-, phenylmethyl-, and phenylscatole, together with indolecarboxylic, dimethylindoleacetic, and dimethylindolecarboxylic acids, were prepared.

Other examples of ring-formation were brought to light by Fischer. In 1883 he found that benzoylacetone is produced by hydrolysing benzoylacetic ester, and, utilising this reaction to prepare *o*-nitrocinnamylacetone, he reduced this to acetonylquinoline,



Furthermore, nitrosoethylaminohydrocinnamic acid gave ethylhydrocarbazostyril,



whilst phenylpyrazoline, $C_6H_5\cdot N<\begin{matrix}N=CH\\ CH_2\cdot CH_2\end{matrix}$, was obtained in 1887 from the phenylhydrazone of acrolein by the action of dilute sulphuric acid.

Carbohydrates, Glucosides, and Depsides.

In the year 1886, chemists recognised two aldohexoses (glucose and galactose), two ketohexoses (fructose and sorbose), and one aldopentose (arabinose); three hexobioses (sucrose, lactose, and maltose) were also known to be definite individuals, and one hexotriose (raffinose). The general structure of glucose and galactose as that of straight-chain pentahydroxyaldehydes, and of fructose as a pentahydroxyketone, also unbranched, had been determined by the work of Kiliani, who relegated to its proper position as a tetrahydroxyaldehyde the pentose, arabinose, erroneously classified by its discoverer as an isomeride of glucose. In these few lines may

be summarised the exact knowledge of crystalline carbohydrates at the time when Emil Fischer approached the subject, and a true measure of the character and magnitude of his constructive achievement may be gained by comparing the foregoing synopsis with the modern classification of the hexose group as represented by projection formulæ.

From that classification it is seen that amongst the sixteen optically active aldohexoses theoretically realisable, twelve have been either synthesised or configurated, or both, by Fischer and his collaborators. His work on ribose made it possible to include *d*-allose and *d*-altrose in the list, of which there thus remain only the *l*-forms of these two aldoses unknown. It involves also the statement that six amongst the eight possible *dl*-aldohexoses have been realised, whence it follows that *l*- and *dl*-allose with *l*- and *dl*-altrose are the only missing members of the twenty-four optical isomerides comprised in the category.

Highly as this admirable web of theory and practice must be valued, its description is not a complete estimate of his finished contribution to aldohexose chemistry. The foregoing computation of possibilities takes no account of the oxide rings now accepted amongst members of this class. His discovery of γ-methylglucoside, and the consequent recognition of cyclic relations distinct from that occurring in α- and β-glucose, have opened the way to a multitude of contingent isomerides, those of *d*-glucose alone numbering ten. Thus Fischer not only elaborated his own sugar chemistry, but he added to this the foundation of a new carbohydrate classification, the development of which will continue to inspire the prosecution of inquiry by generations following his epoch.

The instrument which enabled Fischer to bend his experimental deftness and his theoretical penetration to the purpose of elaborating so delicate a structure was phenylhydrazine. In 1884 he found that with this agent glucose and fructose yield phenylglucosazone, $C_{18}H_{22}O_4N_4$, whilst an isomeride arises from galactose; under similar conditions, maltose and lactose resemble the hexoses, forming individual isomeric osazones, $C_{24}H_{32}O_9N_4$, whilst sucrose, at first indifferent, gradually undergoes partial hydrolysis, generating phenylglucosazone from the products of inversion. Closer study showed that this reaction has the peculiarity of presenting a fully hydrogenised compound, phenylhydrazine, in the light of an oxidising (dehydrogenising) agent. The first product is the phenylhydrazone, which, owing to structural difference between glucose and fructose, is not the same from both sugars; a second molecule

of phenylhydrazine now removes hydrogen from the two phenylhydrazones, yielding two structurally different phenylhydrazones of glucosone, which then undergo condensation with a third molecule of phenylhydrazine to produce the osazone,

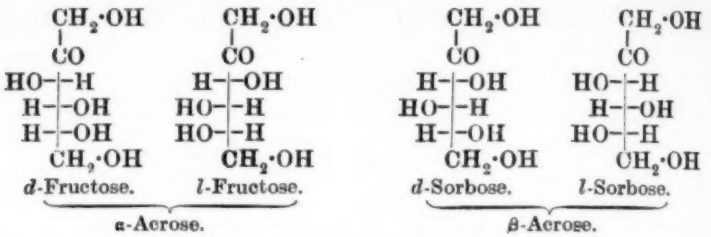
$$HO\cdot CH_2\cdot[CH\cdot OH]_3\cdot C(:N\cdot NHPh)\cdot CH:N\cdot NHPh,$$

common to both.

The extension of this reaction to all aldoses and ketoses, the formation of phenylhydrazides from sugar-acids, and the analogous application of substituted phenylhydrazines, have rendered invaluable service in the identification and isolation of carbohydrates in general, because although the latter, when crystalline, are quite definite in purified form, they are amongst the most difficult materials to manipulate, on account of their tendency to remain as a syrup in mixtures.

Even more important, though less immediately obvious, has been the operation of this process in a synthetical direction. The aspiration artificially to produce grape-sugar is coeval with organic chemistry itself. Liebig had indicated the fascination of this problem, but the first practical step was taken in 1861 by Butlerow, whose methylenitan was a sweet, pale yellow syrup responding to common tests for glucose, but optically inactive and unfermentable by yeast. He polymerised trioxymethylene with hot lime-water, and twenty-five years later Loew, having conveniently modified Hofmann's method of preparing formaldehyde, subjected this compound to the action of cold lime-water, thus producing a syrup which he called formose. In 1888, by means of phenylhydrazine, Fischer showed that formose is a mixture of at least three aldehydic or ketonic polyhydric alcohols, of which one has the composition $C_6H_{12}O_6$, and yields a normal osazone, $C_{18}H_{22}O_4N_4$, also producible from methylenitan.

Fischer himself has stated that the directive influence on his work amongst carbohydrates was the discovery of α- and β-acrose. In 1887, associated with Tafel, he obtained from acrolein dibromide and baryta a syrup which yielded two osazones, isomeric with one another and with phenylglucosazone. These were called α- and β-phenylacrosazone, corresponding to the two synthetical sugars α- and β-acrose, having the composition $C_6H_{12}O_6$. The former sugar he subsequently identified with *dl*-fructose, whilst β-acrose, which he suggested resembled sorbose, has been since recognised as the *dl*-form of that ketose (E. Schmitz, 1913). Thus was accomplished the first definite synthesis, in their *dl*-modifications, of the naturally occurring sugars, fructose and sorbose,

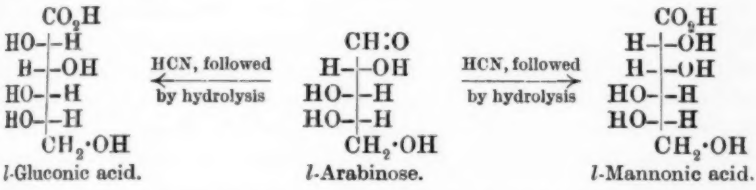


Great as was the advance represented by the acrosazones, the following step might well have daunted a less tenacious investigator. The acroses are optically inactive, and although reducible by sodium amalgam to hexahydric alcohols, of which α-acritol appeared, and was afterwards shown, to be identical with *dl*-mannitol, only 0·2 gram of α-acritol was obtainable from 1 kilogram of glycerol. Use had to be made, therefore, of another reaction, also very tedious experimentally, arising from the study of phenylglucosazone. When this compound is treated with hydrochloric acid, it is hydrolysed completely, leaving the tetrahydroxyketonic aldehyde, glucosone; on reducing this product incompletely with zinc dust in acetic acid, the aldehydic group is hydrogenised selectively before the ketonic, yielding fructose. By applying this process to α-acrosazone, in combination at subsequent stages with Pasteur's methods of separating optical antipodes, the passage from inactive synthetic α-acrose to sugars identical in all respects with *d*-glucose, *d*-fructose, and *d*-mannose was ultimately effected in the following sequence: α-acrose ⟶ *dl*-glucosazone ⟶ *dl*-glucosone ⟶ *dl*-fructose (⟶ *l*-fructose) ⟶ *dl*-mannitol ⟶ *dl*-mannose ⟶ *dl*-mannonic acid ⟶ *d*-mannonic acid (⟶ *d*-gluconic acid ⟶ *d*-glucose) ⟶ *d*-mannose ⟶ *d*-glucosazone ⟶ *d*-fructose.

One step in the above series, namely, the conversion of *d*-mannonic acid into *d*-gluconic acid, deserves attention, because the principle underlying it has been, in Fischer's hands, one of the most fruitful devices in the construction and configuration of new sugars, especially in association with the cyanohydrin synthesis and the reduction of polyhydroxylactones to the aldoses themselves. In 1890 he found that gluconic and mannonic acids are interconvertible, an equilibrium mixture of the two being produced when either is heated with quinoline at 140°. This was a far-reaching discovery, because it afterwards appeared that when any monobasic sugar-acid is heated with quinoline or pyridine, the configuration of the carbon atom adjacent to the carboxylic group becomes inverted or epimerised; gluconic and mannonic acids are consequently said to be epimeric. It was this principle, followed by reducing the lactones of the resulting acids, which enabled

Fischer to produce the artificial sugars *l*-glucose, *d*-talose, and *d*-idose through *l*-mannonic, *d*-galactonic, and *d*-gulonic acids, respectively, and the aldopentoses *l*-ribose and *d*-lyxose through *l*-arabonic and *l*-xylonic acids, respectively.

The cyanohydrin reaction, although actually devised by Kiliani (1885), was widely applied by Fischer, who regarded it as a great advance in the study of the sugar group. A typical example of its application is the conversion (1891) of *l*-arabinose, the dextrorotatory pentose derived from cherry-gum, into *l*-mannonic and *l*-gluconic acids,



l-Gluconic acid. *l*-Arabinose. *l*-Mannonic acid.

This opened a way to the artificial *l*-glucose and *l*-mannose, whilst a similar transformation of *d*-xylose (at that time known as *l*-xylose), the pentose from wood-gum and oat straw, gave *l*-gulose along with *l*-idose. The method was found to be capable of wide extension, and is limited only by the diminishing amount of material available for each succeeding step; thus, the following series were realised by Fischer:

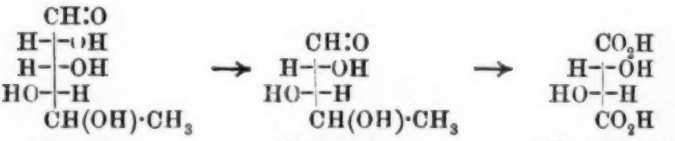
d-Glucose → {α-Glucoheptose, β-Glucoheptose} → {α-Gluco-octose, β-Gluco-octose} → Gluconononose.*

d-Mannose	→ Mannoheptose	→ Manno-octose	→ Mannononose
$C_6H_{12}O_6$	$C_7H_{14}O_7$	$C_8H_{16}O_8$	$C_9H_{18}O_9$
Rhamnose	→ α-Rhamnohexose	→ Rhamnoheptose	→ Rhamno-octose
$C_6H_{12}O_5$	$C_7H_{14}O_6$	$C_8H_{16}O_7$	$C_9H_{18}O_8$

In 1891 an attack was made on the complex problem of configuration, the system of which it has been necessary to assume hitherto in order to give a coherent synopsis within reasonable limits of space. Fischer's procedure was based on the requirements of van't Hoff's theory, from which it follows that the pentahydroxyaldehyde of an unbranched carbon chain, in which five carbon atoms are each associated with one hydroxyl group, should appear in sixteen stereoisomeric forms, eight of these being enantiomorphs of the remainder. The projection formulæ of the sixteen possible aldohexoses are then assembled in conjunction with the eight possible aldopentoses, thus indicating the trihydroxyglutaric acids

* Subsequently extended to glucodecose by Philippe (1911).

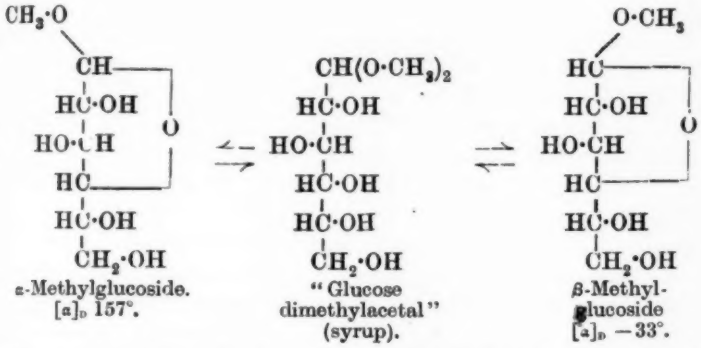
derivable from the latter, the tetrahydroxyadipic acids corresponding with the former, and the structurally symmetrical pentitols and hexitols. Recalling that (1) the cyanohydrin synthesis relates glucose to arabinose, and gulose to xylose, (2) the trihydroxyglutaric acid from xylose is internally compensated, whilst the isomeride from arabinose is optically active, and that (3) saccharic acid arises from both glucose and gulose, but not from any other hexose, it is possible by a process of considered elimination to limit the representation of *d*- and *l*-saccharic acids to two configurations, which are enantiomorphous, leaving the final selection arbitrary. The choice made by Fischer was a happy one, for he was able finally to confirm it in 1896. Having previously (1894) established the configuration of the three carbon atoms proceeding from the aldehydic group in rhamnose, he degraded the sugar by Wohl's method to the corresponding methyltetrose; oxidation of this yielded *d*-tartaric acid, the configuration of which is thus determined:



Just as the internally compensated mucic acid yields, by equally probable disruptions, *dl*-tartaric acid, so saccharic acid, and hence glucose, yield *d*-tartaric acid, thus providing the keystone for Fischer's configurational system.

Although it still simplifies discussion of the aldohexoses to represent them as containing a free aldehydic group, many years have elapsed since this view of their structure was modified. Amongst the earliest known compounds of organic origin are the glucosides, for example, amygdalin, indican, salicin, and myronic acid, owing their class-name to the production of glucose on hydrolysis, which led to their being regarded as ethereal derivatives of this or a related sugar. In 1893 Fischer found that under the influence of hydrogen chloride, glucose combines with methyl alcohol to form the simplest of the glucosides, which he called methylglucoside, and the discovery ultimately elucidated the structure of the sugar-like polysaccharides and of glucose itself. He soon showed this method of synthesis to be general with aldoses and ketoses for the one part, and applicable to the alcohols in which they are soluble, for the other; somewhat similar methods lead from acetone and benzaldehyde to the *iso*propylidene and benzylidene compounds, respectively, products which have been applied to the preparation

of mono-, di-, and tri-methyl derivatives of glucose (Irvine and Scott, 1913). Whilst Fischer indicated the probability of isomerism following the asymmetry of the methoxylated carbon atom, the second methylglucoside was brought to light by van Ekenstein (1894). The mechanism of glucoside formation, in which it seemed convenient to make an arbitrary selection of alternative formulæ for the α- and β-modifications, was then tentatively represented as follows:

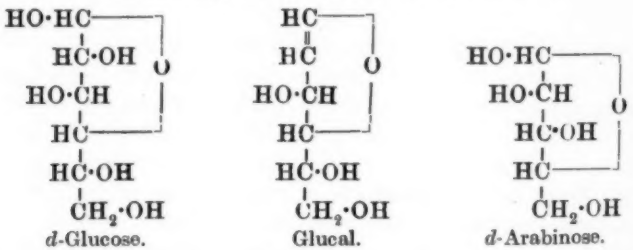


This proposal was in accord with Tollens' γ-oxide (preferably butylene oxide) formula for glucose (1883), and offered a substantial basis for the highly probable explanations, by E. F. Armstrong and by Lowry, of the long observed mutarotation of that sugar. The isolation of glucose in a second form was achieved by Tanret (1896), and it was subsequently accepted that α-glucose, with $[\alpha]_D$ 110°, and β-glucose, with $[\alpha]_D$ 19°, pass, on dissolution in water, to an equilibrium mixture having $[\alpha]_D$ 52·5°. Simon's view (1901) of α- and β-glucose as lower homologues of α- and β-methylglucoside, respectively, has been confirmed by E. F. Armstrong (1903), who correlated each methylglucoside with its parent glucose through the agency of an appropriate enzyme.

There the question remained during the next ten years, when the seed of revolution was sown by Fischer himself. In 1914, J. U. Nef, who had been occupied with a protracted survey of the oxidation undergone by sugars in alkaline solution, challenged the foregoing conception of methylglucoside isomerism by claiming this to be structural in place of steric, and representing the β-form of methylglucoside and of penta-acetylglucose as propylene oxides instead of butylene oxides. Strong arguments against this disturbing proposal were brought forward by Fischer, who simultaneously (1914) described a third methylglucoside. The syrupy companion of α- and β-methylglucoside, hitherto assumed to be the dimethylacetal, was distilled under 0·2 mm. pressure, and

found to be isomeric with them; it resembled them in stability towards alkali and Fehling's solution, but revealed a profound contrast in its behaviour towards acids, which hydrolyse it with extraordinary readiness. Moreover, whilst α-methylglucoside is hydrolysed by maltase (not by emulsin) and β-methylglucoside is hydrolysed by emulsin (not by maltase), γ-methylglucoside is indifferent to both. Fischer conceded the probability of the new glucoside owing its individuality to another form of oxide ring, and was inclined to regard it as a mixture of two or more such isomerides. Both possibilities have been supported by Irvine, Fyffe, and Hogg (1915) from a study of tetramethyl-γ-glucoside and tetramethyl-γ-glucose, in which emphasis is laid on the readiness with which it undergoes condensation with acetone and on the instantaneous oxidation of the new methylglucoside by cold alkaline potassium permanganate, an agent which has no effect on the α- and β-methylglucoside.

This remarkable behaviour towards permanganate invites comparison between the derivatives of γ-glucose and glucal, obtained as the triacetyl derivative on reducing β-acetylbromoglucose (Fischer and Zach, 1913). The conversion of triacetylglucal through the dibromide and the related bromohexose into phenylglucosazone, and the oxidation by ozone to triacetyl-*d*-arabinose (posthumous publication with Bergmann and Schotte, 1920), indicate the first and second carbon atoms as participants in the double linkage of glucal, the relationship of which to *d*-glucose and *d*-arabinose is consequently represented as follows:



d-Glucose. Glucal. *d*-Arabinose.

Glucal is thus a derivative of dihydrofuran, and gains piquancy from having beguiled Fischer into using rare words of enthusiasm when describing its production, which, he declared, "vom Standpunkt der Strukturchemie betrachtet, einer der merkwürdigsten Vorgänge ist, die man bisher in der Zuckergruppe kennen gelernt hat. Sie beweist von neuen, welch wunderbarer Stoff der Traubenzucker ist."

Although Fischer did not commit himself to the particular form of oxide represented by γ-glucose, which has not yet been isolated,

a point has been reached which indicates an ethylene oxide-ring structure for this compound. Before passing to the next branch of the subject, it should be mentioned that the experiments of Böeseken (1913) on the conductivity of boric acid as influenced by polyhydroxy-compounds have thrown some doubt on the accepted configuration of the α- and β-methylglucoside, in which, according to his deductions, the relative positions of the terminal methoxy-group and hydrogen atom should be inverted, and the corresponding rearrangement made in α- and β-glucose.

In conformity with his observations on artificial glucosides, Fischer represented the disaccharides as hexosides composed of the hexoses into which they are resolved by acids or enzymes, one hexose molecule playing the part of the methyl group in the less complex derivatives. Thus maltose and lactose were represented (1893) by the structural formula

$$HO\cdot CH_2\cdot CH(OH)\cdot \underbrace{CH\cdot[CH\cdot OH]_2\cdot CH\cdot O}_{\text{O}}\cdot CH_2\cdot[CH\cdot OH]_4\cdot CH{:}O,$$

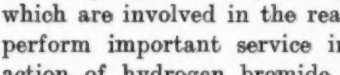
of which the left-hand portion stands for glucose in maltose and for galactose in lactose, whilst the remainder is glucose in both. Moreover, the relationship to the methylglucosides was shown (1894) by their behaviour towards emulsin, which hydrolyses lactose (glucose-β-galactoside) and is without action on maltose (glucose-α-glucoside). Structurally, this agrees with the oxidation of lactose to the monobasic lactobionic acid, $C_{12}H_{22}O_{12}$, and of maltose to the isomeric maltobionic acid (1889), which on hydrolysis yield galactose and glucose, respectively, associated in each case with gluconic acid; moreover, lactosecarboxylic and maltosecarboxylic acids, obtained from the respective disaccharide by the cyanohydrin reaction, yield the above-mentioned hexoses in company with α-glucoheptonic acid when hydrolysed.

Sucrose (cane-sugar), being devoid of aldehydic or ketonic attributes, is at once a fructoside and a glucoside. Fischer's formula (1893), based on that conception, remained unchallenged until his isolation of γ-methylglucoside, when he drew attention to the similar behaviour of these two substances towards acids. Whilst it is assured that the glucose residue has the same type of oxide ring as that of the α- and β-glucosides, his inference that the fructose component is in the γ-form (that is, an ethylene oxide) is supported by Haworth and Law (1916), who adduced new arguments in favour of representing sucrose by a formula in accordance therewith, subsequently confirming (1919) Fischer's original representation of maltose, in which the free aldehydic group is modified to the now conventional butylene oxide. By application of the methylation process, with which the St. Andrews laboratory has

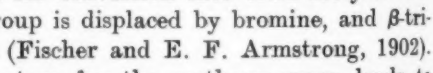
been so conspicuously associated, Haworth (1918) was led to refer Fischer's modified lactose formula (1893) to melibiose.

With so constructive a mind and an armoury of synthetical method so full of weapons, the magnetic problem of elaborating polysaccharide molecules was not likely to be neglected by Fischer. The individuality of *iso*maltose, produced by the action of cold fuming hydrochloric acid on glucose (1890 and 1895), was actively criticised; indeed, it was shown later by E. F. Armstrong that although *iso*maltose is formed in this process, it is accompanied by maltose. Subsequent attempts, however, were based on unassailable foundations. The first of these, in association with E. F. Armstrong (1902), depends on the action of β-acetylchloroglucose on the sodium derivative of galactose, and of β-acetylchlorogalactose on the sodium derivatives of glucose and galactose, the resulting disaccharides forming osazones. The galactosidoglucose closely resembled melibiose in its behaviour towards enzymes and the less delicate chemical agents, but the glucosidogalactose was distinct from lactose; all three resembled the β-glucosides in being hydrolysed by emulsin. From β-acetylbromoglucose and silver carbonate there was produced the octa-acetyl derivative of a disaccharide called *iso*trehalose (Fischer and Delbrück, 1909) from its close resemblance to the carbohydrate which is found in many fungi, and which appears to play in these the part of sucrose in chlorophyllaceous and starch-bearing plants; application of this method to acetylbromolactose gave distinct evidence of a tetrasaccharide being formed (1910), but this compound was not defined.

The group of acetyl–halogen derivatives, typical members of which are involved in the reactions just described, was destined to perform important service in Fischer's later work. When the action of hydrogen bromide on penta-acetylglucose is protracted beyond the period required for conversion into tetra-acetylbromoglucose, a second acetoxy-group is displaced by bromine, and β-triacetyldibromoglucose arises (Fischer and E. F. Armstrong, 1902). Exchange of one halogen atom for the methoxy-group leads to triacetylmethylglucoside bromohydrin, converted by warm baryta into the anhydromethylglucoside, $C_7H_{12}O_5$, which is hydrolysed by acids to anhydroglucose (Fischer and Zach, 1912):



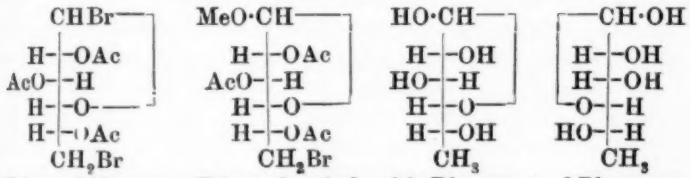
Triacetyldibromoglucose.



Anhydroglucose.

This is crystalline, produces colour in Schiff's reagent, and forms crystalline derivatives with phenylhydrazine, whilst reduction with sodium amalgam gives anhydrosorbitol; anhydrogluconic acid follows oxidation by bromine.

The result of reducing triacetylmethylglucoside bromohydrin is noteworthy also, because it enabled Fischer to elucidate the configuration of the undetermined carbon atom in rhamnose (1912). With Zach, he found that replacement of bromine by hydrogen gave a triacetylmethylglucoside, leading to a methylpentose on complete hydrolysis, proving that the bromine atom in triacetylmethylglucoside bromohydrin occupies the terminal position in the chain. It was further discovered that the new methylpentose is the optical antipode of *iso*rhamnose, which is related to *d*-glucose as is rhamnose to *l*-mannose; thus rhamnose itself is *l*-rhamnose:



Triacetyldibromoglucose. | Triacetylmethylglucoside bromohydrin. | *d-iso*Rhamnose. (*iso*Rhodeose.) | *l*-Rhamnose. (Rhamnose.)

Another remarkable application of acetylbromoglucose led to the synthesis of mandelonitrile-glucoside, which had been obtained by Fischer (1895) as a crystalline, lævorotatory, non-reducing product of hydrolysing with yeast-maltase the disaccharide group in amygdalin without severing the connexion between mandelonitrile and the residual hexose; subsequently, two isomerides were isolated, namely, sambunigrin from the leaves of *Sambucus niger* by Bourquelot and Danjou (1905), and prulaurasin from *Prunus laurocerasus* by Hérissey (1906). Caldwell and Courtauld (1907) recognised all three as β-glucosides, Fischer's being *l*-mandelonitrile-β-glucoside; they regarded sambunigrin as *d*-mandelonitrile-β-glucoside and prulaurasin as the *dl*-form. This forecast was confirmed by the synthesis (Fischer and Bergmann, 1917), which followed the action of silver carbonate on acetylbromoglucose in molten ethyl *dl*-mandelate, the product giving *dl*-mandelamide-glucoside with methyl-alcoholic ammonia; dehydration following resolution gives the mandelonitrile-glucoside in both active forms. It is to be regretted that Fischer himself did not survive to extend this process to the synthesis of amygdalin, which, in 1895, he believed to be "ein Derivat der Maltose oder einer ganz ähnlich construirten Diglucose." One of his last papers, however, describes

the synthesis of glycollonitrile-glucoside (1919), the simplest of the cyanogenetic glucosides, immediately following that of linamarin (from flax), the glucoside of acetonecyanhydrin.

Recalling the manifold parts played by the substituted amino-group in animal and vegetable metabolism, it is a singular fact that so few amino-derivatives of a glucose type have been encountered amongst the products. It was natural, therefore, that glucosamine, isolated from lobster shells by Ledderhose (1878), should attract Fischer's attention, because its empirical relationship to glucose is expressed by a simple interchange of hydroxy- and amino-groups; the actual connexion, however, is elusive, for whilst indirect processes of replacement (Irvine and Hynd) lead variously to *d*-glucose (1912) and *d*-mannose (1914), thus pointing to a Walden inversion, the direct action of nitrous acid involves dehydration in addition to the normal exchange.

The component of lobster shells which yields glucosamine having been called chitin, the sugar-like product, $C_6H_{10}O_5$, from the base and nitrous acid was called chitose; this was oxidised to chitonic acid, $C_6H_{10}O_6$, by Fischer and Tiemann (1894). By the same change they related glucosamine itself to chitamic acid, this being synthesised from *d*-arabinose (1903) by Fischer and Leuchs, who then reduced it to *d*-glucosamine; later in the same year Fischer and Andreae connected chitose and chitonic acid experimentally with hydroxymethylpyromucic acid, $HO\cdot CH_2\cdot \overset{CH-CH}{\underset{\|\quad\|}{C\cdot O\cdot CH}}\cdot CO_2H'$ to which is also related chitaric acid, the product from chitamic (glucosamic) and nitrous acids. Thus chitose, whether regarded as an aldehyde or a butylene oxide, is derived from tetrahydrofuran.

The triacetylmethylglucoside bromohydrin already mentioned was utilised by Fischer in relation to glucosamine. With Zach (1911) he found that ammonia converts it into a β-methylglucoside, in which the amino-group has replaced hydroxyl; but hydrolysis, instead of producing glucosamine, led to an isomeride. It has to be admitted that this branch of sugar chemistry retains a somewhat perplexing aspect, to which the loose nomenclature involved in such expressions as "aminoglucose," "aminofructose," and "methylglucosamine" contributes. This is all the more regrettable in view of the great biochemical interest attaching to glucosamine as a connecting link between carbohydrates and amino-acids.

Before closing this chapter, there remains to be described one of the most remarkable achievements in a series unsurpassed by any organic chemist, namely, the synthesis of tannin. In 1908 Fischer required the chloride of chloroacetyltyrosine for the synthesis of glycyltyrosylglycine, and, being embarrassed by the presence of the

phenolic group, protected this, prior to treatment with phosphorus pentachloride, by substituting the methylcarbonato-group for hydrogen. Immediately applying this device to phenolcarboxylic acids, he prepared *p*-hydroxyhippuric acid (the isomeride of salicyluric acid) with galloyl-*p*-hydroxybenzoic and *p*-hydroxybenzoyl-*p*-hydroxybenzoic acids. Anhydrides analogous to the last-named were rapidly multiplied, and were named "depsides" by Fischer and Freudenberg (1910), owing to the resemblance which many display towards the tannins; in parallel with the polypeptides and polysaccharides, such compounds may be classified as didepsides, tridepsides, etc., typified by the formulæ

$$HO{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H$$

and $(HO{\cdot}C_6H_4{\cdot}CO{\cdot}O)_2{\cdot}C_6H_3{\cdot}CO_2H$. The only recognised natural sources of the depsides are the lichens, of which the best known constituent is lecanoric acid, the depside of orsellinic acid, and in conjunction with his son Hermann, Fischer synthesised lecanoric acid (1903), and represented it as the *p*-ester,

$$HO{\cdot}C\begin{<}\begin{matrix}CH{-}{-}CMe\\ CH{:}C(OH)\end{matrix}\end{>}C{\cdot}CO{\cdot}O{\cdot}C\begin{<}\begin{matrix}CH{-}{-}CMe\\ CH{:}C(OH)\end{matrix}\end{>}C{\cdot}CO_2H,$$

of which evernic acid is the *p*-methyl ether.

The history of the tannins dates from the eighteenth century, but from the standpoint of this review the earliest year of importance is 1852, when Strecker deduced the formula $C_{27}H_{22}O_{17}$ for gallotannic acid or gall-nut tannin, which he regarded as a compound of grape-sugar and gallic acid in the molecular proportion 1:3. For half a century there prevailed a conflict of opinion as to the presence of a glucose residue, the production of sugar on hydrolysis being denied by several chemists, and the proportions in which it was obtained by the followers of Strecker varying much amongst themselves. In consequence of this uncertainty, Schiff's view (1871) of tannin as consisting principally of digallic acid preponderated until recently. The conductivity measurements by Walden (1897), however, paved a way for the unquestionable differentiation of the two materials by Fischer, who synthesised digallic acid in 1908 and found it to be crystalline, although astringent; moreover, in 1912, having adopted a method of purifying the principal constituent of Chinese tannin and of producing specimens having constant optical activity, he and Freudenberg proceeded to show that when hydrolysed with sulphuric acid it yields 7 to 8 per cent. of glucose, an amount which they regarded as probably too low in view of the extended period occupied in completing the operation. They then expressed the opinion that the principal constituent of tannin is not a glucoside, but a sugar

ester comparable with pentabenzoylglucose, in which the acyl group is that of digallic acid. Expressed by the formula

$$C_6H_7O_6[C_6H_2(OH)_3\cdot CO\cdot O\cdot C_6H_2(OH)_2\cdot CO]_5,$$

such a compound having the molecular weight 1700 would yield 10·6 per cent. of glucose and 100 per cent. of gallic acid on hydrolysis.

At the time of making this very penetrating speculation, they synthesised pentagalloylglucose, which they found to be a tannin, not identical with gall-nut tannin, but resembling it closely in taste, solubility, amorphism, optical activity, and feeble acidity; moreover, it precipitates gelatin and alkaloids, becomes gelatinous with arsenic acid, and develops colour with ferric chloride. In the course of this investigation they prepared hepta(tribenzoylgalloyl)-*p*-iodophenylmaltosazone, a freak molecule of gigantic dimensions (M.W. 4021), vastly exceeding those of any other synthetic product.

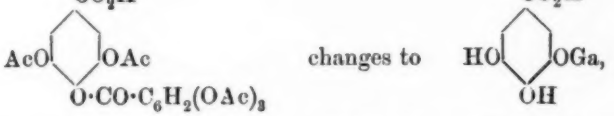
Valuable as the use of methylcarbonato-derivatives had proved, it did not suffice to perfect the aim in view, namely, to synthesise the main principle of Chinese tannin. This was accomplished in 1918, following the observation that the corresponding acetyl compounds are superior to the methylcarbonato-derivatives for depside production. In making this advance, Fischer explained that the acetylated phenolcarboxylic acids would certainly have been used much earlier had not he been misled by the statements of previous workers as to the difficulty of removing the acetyl group, which actually proceeds quite smoothly. The chloride of penta-acetyl-*m*-gallic acid, unlike the methylcarbonato-derivative, is crystalline, and with β-glucose yields the compound,

$$C_6H_7O_6[C_6H_2(OAc)_3\cdot CO\cdot O\cdot C_6H_2(OAc)_2\cdot CO]_5,$$

which is de-acetylated by cold aqueous sodium hydroxide at 0°, giving penta(*m*-digalloyl)-β-glucose (Fischer and Bergmann, 1918). The resemblance between this artificial tannin and the principal constituent of Chinese tannin is much closer than that offered by pentagalloylglucose; the two materials are, in fact, indistinguishable, excepting with respect to optical activity, and the same remark applies to penta(*m*-digalloyl)-α-glucose, the recorded $[\alpha]_D$ in water being 43·8° and 42·3° for the derivatives of α- and β-glucose, respectively, and 70° for the purified Chinese tannin. The correspondence between the potassium salts (1919) is even closer, those from Chinese tannin, pentadigalloyl-α-glucose, and pentadigalloyl-β-glucose having $[\alpha]_D$ 46·3°, 56·6°, and 33·7° respectively.

It is therefore justifiable to claim that gallotannic acid or gall-

nut tannin has been synthesised. Incidentally to this remarkable conclusion, it was observed that when acylated *p*-digallic derivatives are hydrolysed, even by the most delicate methods, the galloyl nucleus is transferred from the para- to a meta-hydroxy-group; for instance, under the influence of alkalis, ammonia, or mineral acids,



and hence penta-acetyl-*p*-digallic acid yields *m*-digallic acid.

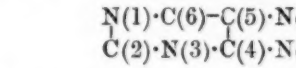
Thus was brought to a conclusion, in the closing months of his darkened life, that illustrious chapter of chemistry with which Emil Fischer first drew on himself the admiration of his contemporaries. It represents the fruit of thirty-five years' unremitted labour and the ripening of an intellectual and experimental technique but rarely developed in the history of scientific endeavour. Begun in the vigorous days of his early manhood, when domestic happiness suffused his professional activity and adorned the promise of a brilliant career, it supported him in his first tragedy, stirred to the utmost the deep resources of his mind, and finally solaced those concluding years in which he was compelled to witness the pillars of Prussianism crumbling at the feet of his disillusioned and bewildered countrymen.

Purine Derivatives.

Some of the most notable figures in chemical history have devoted themselves to the problems which cluster round uric acid and its allies. Scheele, Bergmann, Fourcroy, Prout, Liebig, Mitscherlich, Wöhler, von Baeyer, Strecker, Stenhouse, and Gerhardt are found in the list of names connected with the subject, and to a high place of honour in this galaxy Fischer is most assuredly entitled. Between 1881, when he resolved caffeine into methylcarbamide and dimethylalloxan, and 1914, the year in which he synthesised a nucleotide in the form of theophylline-*d*-glucosidephosphoric acid, the literature was enriched by a succession of systematic observations which reached a climax in 1898, when he derived purine from uric acid by means of indirect deoxidation.

Although uric acid was discovered in 1776, fifty-eight years elapsed before its composition was established, and four years later, in 1838, Liebig and Wöhler published their comprehensive survey of its oxidation products; the true nature and significance of these

were revealed by von Baeyer's experiments, described in 1863 and 1864, thus preparing the ground for the now accepted constitutional formula proposed by Medicus in 1875. This was confirmed in 1888 by Behrend and Roosen, whose synthesis of uric acid, unlike its predecessors, was achieved by definite steps, a feature also of that by Fischer and Ach in 1895. The modern system of notation, according to which the diureides are classified as derivatives of purine and referred to the bicyclic nucleus,

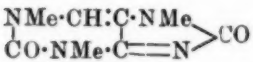


was promulgated by Fischer in 1897, thirteen years after his introduction of the name (*purum* : *uricum*) in connexion with the methyl derivative. The relationship

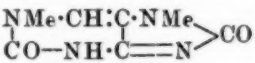
$C_5H_4N_4O_3$	$C_5H_4N_4O_2$	$C_5H_4N_4O$	$C_5H_4N_4$
Uric acid. (2 : 6 : 8-*Trioxypurine.*)	Xanthine. (2 : 6-*Dioxypurine.*)	Hypoxanthine. (6-*Oxypurine.*)	Purine.

was thus consolidated, the catalogue of purine derivatives contributed by Fischer and his collaborators prior to 1900 embracing upwards of 130 individuals.

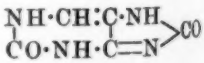
The readiness with which caffeine lends itself to experimental treatment led Fischer to open attack on the problem of uric acid by first elucidating the constitution of that base, and a preliminary communication thereon appeared in 1881. His introductory work dealt also with xanthine, theobromine, and guanine. By oxidising aqueous caffeine with chlorine, Rochleder had obtained amalic acid (tetramethylalloxantin), which Fischer showed to be preceded by chlorocaffeine, and to arise from the action of hydrochloric acid on dimethylalloxan; the latter substance and methylcarbamide were found to be the principal products of oxidising caffeine in the manner indicated, and it was proved convenient to prepare chlorocaffeine by acting with the halogen in absence of water. Similarly, theobromine was oxidised to methylcarbamide and methylalloxan, showing that when caffeine is produced by methylating theobromine, the entrant methyl group becomes attached to the alloxan ring. Next, improving the preparation of xanthine from guanine, Fischer oxidised it to alloxan and carbamide, and by acting on the lead derivative with methyl iodide obtained theobromine; on the basis of these and subsidiary experiments, he assigned the following constitutional formulæ (see, however, later):



Caffeine.



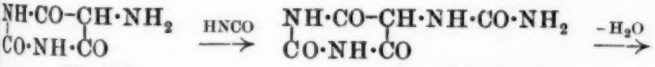
Theobromine.



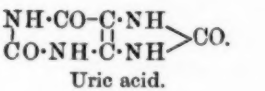
Xanthine.

It is noteworthy that even at this period (1882) the products interested him from the standpoint of relation between chemical constitution and physiological action; moreover, Dr. Ludwig Knorr is mentioned as his assistant.

In 1864 Strecker stated that Rheineck had reduced uric acid to xanthine and sarcine (hypoxanthine) by means of sodium amalgam, but he never mentioned the subject again, and did not include the observation in his "Lehrbuch." Fischer found that uric acid is not changed by sodium amalgam, and likewise that, contrary to the statement of Kossel, hypoxanthine is not converted into xanthine by nitric acid. Thus in 1884, uric acid, xanthine, and hypoxanthine, so similar in origin, behaviour, and composition, had no direct experimental connexion with one another. In that year Fischer studied methyluric acid in the hope of establishing the foregoing relationship with respect to the methyl derivatives of xanthine and hypoxanthine. To the existing compound, which gives carbamide and methylalloxan on oxidation, he added an isomeride, which yields methylcarbamide and alloxan when oxidised, and is converted by phosphorus pentachloride into trichloromethylpurine, from which methyluric acid can be regenerated. Complementary also to the dimethyluric acid, which gives methylcarbamide and methylalloxan when oxidised, he discovered an isomeric dimethyl derivative yielding cholestrophan (dimethylparabanic acid). It was thus established that, in addition to the ring which appears in the form of alloxan (mesoxalylcarbamide), uric acid contains two imino-groups associated with one another as in carbamide itself. The methylation of uric acid was then carried to the trimethyl derivative, apparently isomeric with hydroxycaffeine (see later), and to tetramethyluric acid, isomeric with methoxycaffeine, but having all the methyl groups attached to nitrogen, thus indicating the presence of four imino-groups in uric acid, as required by the structural formula previously advanced by Medicus. This was further confirmed in 1895, when Fischer and L. Ach added the final step in the transformation,



Uramil. Pseudo-uric acid.



Uric acid.

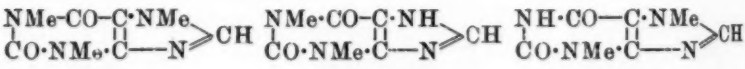
Then, applying this process to dimethyl*pseudo*uric acid, they produced a third dimethyluric acid, convertible by phosphorus penta-

chloride into chlorotheophylline, from which theophylline arises on exchanging halogen for hydrogen:

Dimethyluric acid. Chlorotheophylline.

This completed the synthesis of theophylline, and, incidentally, of caffeine.

Then arose a situation which is rarely encountered in the course of Fischer's investigations. He was compelled by his own experiments to revise the structural formulæ which he had assigned to xanthine and its derivatives, caffeine, theobromine, and theophylline. In 1895 he had produced a fourth dimethyluric acid by exchanging halogen for hydroxyl in bromotheobromine, and the simplicity of this procedure did not harmonise with the profound structural rearrangement apparently involved. A more rigid examination of hydroxycaffeine, believed to be isomeric with trimethyluric acid, showed it to be identical with that substance, and by varying the conditions of methylation, tetramethyluric acid was obtained from it. Moreover, hydroxycaffeine was produced without difficulty from the corresponding trimethyl*pseudo*uric acid, and finally by direct methylation of uric acid itself. In consequence of these discoveries, Fischer modified his previous expressions and assigned the following in 1897:

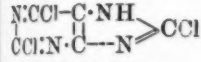


Caffeine. Theophylline. Theobromine.

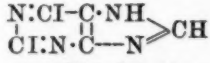
During his investigation of methyluric acid in 1884, Fischer had found that phosphorus pentachloride in presence of the oxychloride easily replaces two, and finally all three, oxygen atoms by chlorine, producing trichloromethylpurine. In 1897, assisted by L. Ach, he converted uric acid by the same process into 8-oxy-2:6-dichloropurine, reducible to 8-oxypurine isomeric with hypoxanthine, and convertible by ammonia into 6-amino-8-oxy-2-chloropurine; this was reduced to 6-amino-8-oxypurine isomeric with guanine, from which nitrous acid produced 6:8-dioxypurine isomeric with xanthine. The complete replacement of oxygen by chlorine was much more difficult, but by heating 8-oxy-2:6-dichloropurine with seventy parts of phosphorus oxychloride at 150°, Fischer obtained trichloropurine, a basic substance giving the 7- and 9-methyltrichloropurines on methylation, and providing him with material for completing the synthesis of hypoxanthine

(6-oxypurine), xanthine (2:6-dioxypurine), adenine (6-amino-purine), and guanine (2-amino-6-oxypurine).

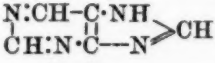
The goal towards which Fischer first directed himself in 1884 was now reached. Purine, the parent of the group, and on which the nomenclature and notation of the whole series had been based, lay open to isolation; the accomplished facts were described in 1898. Trichloropurine was reduced in two stages, the first depending on the action of hydrogen and phosphonium iodides at 0° and producing 2:6-di-iodopurine, from which purine itself was obtained by the action of zinc on a boiling aqueous solution:



2:6:8-Trichloropurine.



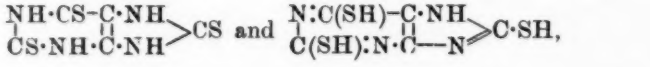
2:6-Di-iodopurine.



Purine.

Purine was thus found to be a definite entity, amphoteric in character and harmonising completely with its position in the series.

Attention has been drawn to the difficulty with which uric acid is converted into trichloropurine, and to the fact that only one halogen atom in this compound is exchanged for oxygen by alkali hydroxides. Alkali sulphides, however, rapidly displace all three, producing trithiopurine (1898), and of the two tautomeric formulæ,



Fischer preferred the latter. Another by-path was pursued in 1900, when he prepared 9-phenyluric acid from the corresponding phenyl*pseudo*uric acid, which results from the action of phenylcarbimide on uramil; this was followed by 9-phenylpurine.

The series of six dimethyluric and four trimethyluric acids was completed with assistance from F. Ach by the preparation of 1:9-dimethyl- and 1:7:9-trimethyluric acids, but the monomethyl derivatives presented a curious anomaly. According to the lactame formula for uric acid, there should be four methyluric acids, in which the alkyl group occupies the position 1, 3, 7, or 9 respectively, but the existence of two additional ones was claimed. Of these six methyluric acids, Fischer and F. Ach (1899) showed that three appear to have the alkyl group attached to the same nitrogen atom, numbered 3 in the purine nucleus, giving the same methylallantoin (on oxidation) and tetramethyluric acid. The mystery remained unsolved until 1916, when an independent examination of the materials by Biilmann and Bjerrum, Biltz and Heyn, showed that the supposed difference is due to the contamination of

3-methyluric acid with a varying proportion of the 9-methyluric acid.

Although for many years displaced from his experimental attention, the purines became involved in Fischer's synthesis of nucleotides. It has already been seen that acetylbromoglucose is a valuable agent in elaborating glucosides, and in 1914, assisted by B. Helferich, he brought this compound into action with the silver derivative of numerous oxypurines, producing the *d*-glucosides of theophylline, theobromine, adenine, hypoxanthine, and guanine; the outstanding feature of these compounds is the readiness with which they are hydrolysed, thus being distinguished from derivatives of glucosamine. Finally, by adding a cold mixture of phosphoryl chloride and pyridine to a solution of theophylline-*d*-glucoside in pyridine, he prepared, later in the same year, theophylline-*d*-glucosidephosphoric acid, the first synthetic nucleotide.

Amino-acids, Polypeptides, and Proteins.

In view of their extent and the far-reaching biochemical conclusions which have been based on them, the labours of Emil Fischer in the region of proteins will make the same appeal to the imagination and evoke the same delight in craftsmanship as his activities amongst carbohydrates. Owing to the much greater complexity of the subject, however, the intrinsic results may at first appear less complete; but the relative success is equally remarkable, because his treatment of this branch reveals the skilful manipulation of sensitive materials, the deft application of experimental indications, and the constructive diligence in synthetic achievement already so admirably displayed by his earlier work.

The amino-acids bear to the proteins a relationship recalling that of a hexose to a polysaccharide. Accordingly, it was with those materials that Fischer began, in 1899, experiments which were destined to reveal the chemical nature of the proteins themselves, and to furnish material which indicates, at least, the manner in which lifeless protein may ultimately be synthesised. It had then been recognised that nine amino-acids, three diamino-acids, and cystine were obtainable by hydrolytic or enzymic disruption of protein molecules; the synthesis of glycine, alanine, α-aminovaleric acid, leucine, aspartic acid, glutamic acid, phenylalanine, and tyrosine, all in their *dl*-forms, had been accomplished either by Strecker's method or by substituting the amino-group for halogen in the respective α-chloro- and α-bromo-acids, but serine, although discovered in 1865, was not synthesised until 1902 (Fischer

and Leuchs). The resolution of these products into their optically active components had been limited by their amphoteric nature, and was easy only in the case of aspartic acid, Piutti having shown, in 1887, that asparagine is resolved by simple crystallisation from water.

By suppressing the basic aspect of the amino-acids, and thus encouraging their capacity to form recrystallisable salts with the natural alkaloids, strychnine and brucine, Fischer and his collaborators first resolved into their antipodal components the *dl*-forms of alanine, α-aminobutyric acid, leucine, α-amino-*n*-caproic acid, phenylalanine, tyrosine, aspartic and glutamic acids, valine, serine, *iso*serine, and proline. The device by which this was effected consists in benzoylating (1899), formylating (1905), and, in the case of serine, *p*-nitrobenzoylating (1906) the amino-group, resolving the *dl*-acylamino-acid by recrystallising its salts with strychnine or brucine, and hydrolysing separately the antipodal benzoyl, formyl, or *p*-nitrobenzoyl derivative of the *d*- and *l*-amino-acid. In this manner were accumulated, in greater quantity and variety, optically active units, which thus became available as building materials for the construction of polypeptides approaching the peptones in physical characteristics.

The foregoing acyl derivatives, in common with others depending on the reactivity of the amino-group with phenylcarbimide and benzenesulphonyl chloride, are useful for identification as well as isolation of their parent compounds, but some still better for the former purpose followed from combination with β-naphthalene-sulphonyl chloride (1902); the resulting derivatives are formed in good yield, are sparingly soluble, and crystallise sufficiently well to facilitate the recognition of hydroxyamino-acids and even poly-peptides themselves, in addition to the compounds from which the latter are built. Thus, to a minor extent, β-naphthalenesulphonyl chloride assumes the part played by phenylhydrazine in the sugar group, affording an instrument for isolating freely soluble and elusive substances.

Early attempts to explain the structure of proteins had been hampered by experimental obstacles to the separation of amino-acids produced in such complex mixture by hydrolysis; with the exception of tyrosine and cystine, which are sparingly soluble in water, the major portion of the mixture remains as a syrup after the principal constituent has crystallised. It was thus a practical advance of the first magnitude which Fischer made as the result of his inquiry (1900) into the esters which, owing to the suppression of the carboxylic function, have the properties of aliphatic amines; this feature had been recognised in 1883 by Curtius, whose process

for isolating the esters was modified by Fischer and applied by him to separating the amino-acids in a complex mixture through fractional distillation. The procedure offers considerable experimental difficulty, but it is the only one which has been really successful, and its purpose has now been achieved with a large number of elaborate molecules. Edestin, elastin, fibrin, globin, gluten, keratin, and the albumins of egg, serum, and milk are examples of the zeal with which Abderhalden has pursued this line of inquiry, whilst Osborne and his collaborators, by similar methods, have ascertained the component amino-acids of amandin, excelsin, gliadin, glycinin, hordein, phaseolin, and zein. Particularly to Fischer himself is due the resolution of the fibroin produced by silkworms and spiders, incidentally emphasising the remarkable biological fact that there is only slight chemical difference between the synthetic products of two creatures whose diet is so vastly divergent. He showed (1907) that the silk of the Madagascar spider gives, per cent.: glycine 35·1, *d*-alanine 23·4, *l*-leucine 1·7, *l*-tyrosine 8·2, proline 3·7, *d*-glutamic acid 6·1, diamino-acids (calculated as arginine) 5·2, ammonia 1·1, and fatty acids 0·6; thus the principal difference is the large proportion of glutamic acid, which has not been derived from ordinary silk, and the absence of serine.

Some indication of the nature and variety of the chemical units from which the proteins are constructed having been given, attention must now be directed towards the notable attempts made by Fischer artificially to elaborate protein molecules from their component elements. It is a noteworthy feature of the proteins that, in spite of certain basic properties and the prompt appearance of the amino-group on hydrolysis, the amount of nitrogen liberated by nitrous acid is trifling compared with the percentage of that element in the original material. This fact, in conjunction with the early recognition of hippuric acid as benzoylglycine, gives a clue to the manner in which amino-acid molecules are associated in the natural products now under consideration, and several observations by the earlier investigators confirm it. The simplest of these is the production of a bimolecular anhydride of glycine by the auto-condensation of the ethyl ester (Curtius, 1888). Two such anhydrides are conceivable,

$$\begin{matrix}\mathrm{NH\cdot CH_2\cdot CO}\\ \mathrm{CO\cdot CH_2{-}NH}\end{matrix}$$

Diketopiperazine.

and $\mathrm{NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H}$

Glycylglycine.

according to the proportion of water eliminated, and Curtius's anhydride belongs to the former class. In 1900 Fischer obtained

analogous products from the esters of α-aminobutyric, α-amino*iso*-caproic (leucine), and α-amino-*n*-caproic acids, and classified them as diketopiperazines, in consequence of an observation by Mylius (1884), who prepared the anhydride of sarcosine. Realisation of the alternative type, glycylglycine, came in 1901, when, in conjunction with Fourneau, Fischer hydrolysed diketopiperazine without detaching the two glycine molecules, and thereafter began that astonishing series of elaborations which culminated (1907) in the synthesis of an octadecapeptide,

$$NH_2\cdot CH(C_4H_9)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH(C_4H_9)\cdot CO\cdot [NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH(C_4H_9)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH_2\cdot CO_2H,$$

composed of glycine (15) and *l*-leucine (3) molecules, and having the molecular weight 1213. The name "polypeptide" was adopted to emphasise the similarity to peptones displayed by the properties of the new class, whilst recalling the manner in which polysaccharides are compounded of simple carbohydrate molecules.

Subsequently to the process just reviewed, namely, arrested hydrolysis of a cyclic anhydride, two general methods were employed by Fischer to effect these imposing syntheses. Briefly stated, they depend on elongating the amino-acid chain at the basic and acidic terminals respectively. By the former mechanism a chloro- or bromo-acyl chloride, acting on the amino-acids (or polypeptides already synthesised therefrom), produces a halogen derivative, which only needs treatment with ammonia to become converted into the corresponding amino-compound, for instance, glycylalanine:

$$CH_2Cl\cdot COCl + NH_2\cdot CHMe\cdot CO_2H \longrightarrow CH_2Cl\cdot CO\cdot NH\cdot CHMe\cdot CO_2H.$$

In this manner, the glycyl, alanyl, α-aminobutyryl, leucyl, phenylglycyl, phenylalanyl, and prolyl (α-pyrrolidinecarboxylic) groups were introduced (1903—1905).

The complementary process arose from the discovery (1904) that chlorides of halogenated acylamino-acids could be prepared by the action of phosphorus pentachloride on the acid dissolved in acetyl chloride; when such acyl chlorides act on the ester of an amino-acid or a polypeptide, the product only requires to be hydrolysed and treated with ammonia in order to yield the higher polypeptide corresponding to its component molecules:

$$\underset{\text{Bromo}\textit{iso}\text{capronylglycyl chloride.}}{C_4H_9\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot COCl} + \underset{\text{Glycylglycine ester.}}{NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et}$$

$$\longrightarrow C_4H_9\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$$

$$\longrightarrow \underset{\text{Leucyldiglycylglycine.}}{C_4H_9\cdot CH(NH_2)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot CO_2H.}$$

Although this process is elastic, there presented itself an experimental obstacle to great extension, namely, the solubility of many such acyl chlorides in acetyl chloride, and the consequent difficulty in separating them from solution without decomposition. This was overcome by preparing the acyl chlorides of the amino-acids or of the polypeptides themselves; these chlorides, having the general formula $R{\cdot}CH(NH_3Cl){\cdot}COCl$, are also ammonium chlorides, and are generally not readily soluble in acetyl chloride. As they act smoothly on the esters of amino-acids and polypeptides, the device has been a most fruitful one, and particularly useful in application to the *d*- and *l*-amino-acids, with consequent synthesis of optically active polypeptides. Straightforward as these reactions appear in description, they represent a very remarkable feat experimentally, the rigid exclusion of water being necessary throughout.

Another advantage offered by this process is the facility with which it can be applied to elaborating polypeptides of diverse units, such as glycyl-*d*-alanylglycyl-*l*-tyrosine (1908), isomeric with the tetrapeptide which Fischer obtained in the previous year from silk hydrolysis, and herein lies the connecting link between these notable synthetic operations and the peptones arising from incomplete disruption of protein molecules.

The far-reaching consequence of the method provided by Fischer to separate the components of an amino-acid mixture has already been indicated, but the esters thus isolated were, until 1902, those of amino-acids only, unassociated with polypeptides. In that year, however, assisted by Bergell, he produced from silk fibroin, by successive hydrolysis with hydrochloric acid, trypsin and baryta, a dipeptide which appeared to be glycyl-*d*-alanine, although it could not be identified with the synthetic product; but in 1906, with Abderhalden, he obtained from the same source a methyldiketopiperazine, $\begin{matrix}NH\text{---}CH_2{\cdot}CO\\ |\qquad\quad |\\ CO{\cdot}CHMe{\cdot}NH\end{matrix}$, identical with that producible from glycine and *d*-alanine, thus indicating that glycyl-*d*-alanine is amongst the degradation products of silk fibroin. Then followed the recognition of glycyl-*d*-tyrosine (silk fibroin), glycyl-*l*-leucine and *d*-alanyl-*l*-leucine (elastin), *l*-leucyl-*d*-glutamic acid (gliadin), and glycyl-*d*-alanylglycyl-*l*-tyrosine (silk fibroin).

It is obvious that the field of investigation opened by the foregoing experiments is limited only by material considerations, and an interesting calculation of the possibilities presenting themselves was made by Fischer in 1916. According to this, the octadecapeptide has 816 possible isomerides, whilst a polypeptide comprising 30 amino-acid molecules, of which 5 are glycine, 4 alanine,

3 leucine, 3 lysine, 2 tyrosine, 2 phenylalanine, and 13 various other descriptions, has a number of possible isomerides reaching $1{\cdot}28 \times 10^{27}$. In these computations it is assumed that the mechanism of linking the amino-acid groups is limited to that of glycylglycine, but further complexity would arise from alternative junctions, such as that of diketopiperazine, the possibility of which was not excluded by Fischer. Moreover, he recognised that hydroxyamino-acids, such as tyrosine, serine, and hydroxyproline, may participate in the linkages peculiar to esters and ethers. Although the aggregate number of synthetic polypeptides must be well in excess of 200, this only serves to illuminate the gulf which still separates the chemical investigator from his goal. That Fischer appreciated this baffling factor to the fullest extent appears not only from his frequent references thereto, but also from the nature of his later synthetic operations. Following the octadecapeptide, these were directed more particularly to the association of optically active *Bausteine*, which were varied amongst themselves as much as possible with a view to synthesising those peptide fragments which possess the natural configuration, a property to be revealed by zymolysis. Drechsel's iodogorgonic acid from coral (1896), having been found identical with 2:5-iodotyrosine, was linked with glycine (1908), whilst *d*-valine, α-aminostearic acid, β-aminobutyric acid, α-methyl*iso*serine, *l*-histidine, and *l*-proline were introduced also in the latter year, followed by *l*-cystine and *l*-phenylalanine; polypeptides containing *d*-tryptophan, *iso*serine, lysine, arginine, asparagine, *d*-glutamic acid and aspartic acid as components have since been prepared.

Although the simpler polypeptides are crystalline, and in that aspect bear no resemblance to the proteins, their tendency to amorphism increases with molecular weight, and aqueous solutions of the more complex ones are opalescent, yielding precipitates with ammonium sulphate, phosphotungstic acid, and tannin. Naturally, they do not respond to the colour test depending on tryptophan and tyrosine when those groups are absent, but they give the biuret reaction, and these features, in conjunction with their behaviour towards enzymes (see later), afford the strongest possible evidence in support of the protein diagnosis outlined by this chapter of Fischer's work. One passes to the next with the sensations of an explorer liberated from the perplexing entanglements of a dense forest to find himself on the shore of a limitless ocean.

Zymo-chemistry.

Since chemistry emerged from the crucible of alchemy, its association with biology has become increasingly intimate. Viewed materially, life is a process in which alternations of growth, decay, and regeneration present themselves in the light of chemical transformations, delicate, manifold, and inscrutable. Within the tissues of a living organism there proceed perpetual analyses and syntheses of which we gain an occasional glimpse, but cannot hope, by the comparative brutality of the test-tube, to stage the likeness. Nature's agents are photosynthesis and enzyme action, magic wands which transform carbon dioxide, water, and nitrogen into carbohydrates, fats, and proteins, and which, having synthesised these materials in plants, empower animals to analyse them and assimilate the products of disintegration. In the words used by Fischer during his Faraday Lecture, 1907, "the ultimate aim of biochemistry is to gain complete insight into the unending series of changes which attend plant and animal metabolism."

Having now reviewed some of his most important contributions to our knowledge of the building materials, and proceeding to consider the use which he made of the enzymes themselves, it is noteworthy that this began on a by-road of the great thoroughfare which he cut through the realm of carbohydrates. In 1889, having shown that the "seminose" produced by Reiss from vegetable ivory (*Phytelephas macrocarpa*) is identical with mannose, he isolated alcohol from the products of fermenting that sugar, and in the following year cultivated yeast in solutions of *dl*-mannose and α-acrose (*dl*-fructose); in each case, the *d*-component was devoured, and thus *l*-mannose and *l*-fructose were isolated.

In 1894, assisted by Thierfelder, Fischer made a comparative study of natural and synthetical monosaccharides in respect of their attitude towards various families of yeast, from which it followed that whilst *d*-mannose, *d*-fructose, and, in lower degree, *d*-galactose resemble *d*-glucose, the yeasts are indifferent towards *d*-talose, *l*-mannose, *l*-glucose, sorbose, *l*-arabinose, rhamnose, α-glucoheptose and α-gluco-octose. This indicated that the fermentative principle of yeast is an asymmetric agent which is capable of attacking only those molecules of which the geometrical form does not differ too widely from that of *d*-glucose. It suggested also the possibility that, by persuasive tactics, a reluctant yeast might be tempted ultimately to modify its inherited taste and to accept as nutriment a sugar with which the asymmetry of its enzyme was not originally harmonious. This possibility has not yet been definitely realised.

Pasteur's notable discovery in connexion with *Penicillium* was

thus recalled, and, on extending the inquiry to natural and artificial glucosides, Fischer found that these materials arrange themselves into distinct groups in respect of their behaviour towards air-dried yeast extract (maltase) and emulsin, the *α*-*d*-glucosides being hydrolysed by maltase and indifferent to emulsin; the latter, however, hydrolyses the *β*-*d*-glucosides, which are not attacked by maltase, both enzymes being without action on *l*-glucosides, *d*-galactosides, arabinosides, xylosides, rhamnosides, and gluco-heptosides. Maltose is hydrolysed by the yeast extract, not by emulsin, whilst lactose displays the converse behaviour. It was by observations such as these that Fischer was led to emphasise the close relationship connecting the configuration of a sugar with that of the enzyme which attacks it, and to depict the mechanism of enzyme action by the simple analogy of a lock and key.

In the same year one of the many rocks which await the unwary voyager on this particular ocean was charted by Fischer. The "invertase" of that period was precipitated by alcohol and did not hydrolyse maltose, but Fischer replaced the solid material by an aqueous extract of air-dried (Frohberg) yeast; this does hydrolyse maltose, but neither the disaccharide nor *α*-methyl-glucoside is affected by an aqueous extract of the fresh yeast which has not been dried, although cane-sugar is inverted. After being ground with powdered glass, the same yeast yields an extract capable of hydrolysing maltose and *α*-methylglucoside, but the action is much more feeble than when the glucosides are left in contact with the suspended organism which has been narcotised. In consequence of divergent observations by G. H. Morris, it was found that complications are introduced by the proportion of chloroform employed, and this led to the use of toluene in its place.

The foregoing imbroglio emphasised the importance of specifying an enzyme by some reference to its origin, because an enzyme from one source is almost invariably associated with others, differing from those which accompany it when the origin is different. Fischer showed that whilst the extract of dried yeast hydrolyses both cane-sugar and maltose, the enzyme producing the latter effect cannot be invertase, because individual yeasts which contain invertase fail to hydrolyse maltose; moreover, invertase purified by alcohol is also indifferent towards this disaccharide. The specific maltoclastic enzyme had been called glucase by other workers, and it was for this name that Fischer substituted maltase, previously used by Bourquelot.

Lactose, which is indifferent towards brewer's yeast, is fermented by the milk-sugar yeasts, *S. Kefir* and *S. Tyrocola*. It had been claimed by Beyerinck, on somewhat slender evidence, that these

contain an enzyme, lactase, capable of hydrolysing lactose prior to fermentation; this was established by Fischer, who showed that the same result, intensified, was produced by kefir granules. Other observations of this period related to trehalose and melibiose, and it appeared to follow as a general conclusion that disaccharides are not fermented as such, but only in consequence of a preliminary hydrolysis by a specific enzyme.

In 1898 Croft Hill showed that the hydrolytic action of yeast maltase is reversible, a disaccharide being produced when that enzyme acts on glucose in concentrated solution; subsequently, Emmerling regenerated amygdalin by the action of yeast maltase on a mixture of mandelonitrile-glucoside and glucose, whilst Hanriot revealed the esterifying effect of lipase. In 1902 Fischer and E. F. Armstrong subjected a mixture of glucose and galactose to the action of kefir lactase, and, having removed the unchanged monosaccharides by fermentation, found in solution a disaccharide, which they called *iso*lactose, observing that in its behaviour towards enzymes it stands midway between lactose and melibiose; moreover, the kefir lactase which links its generators has the power to separate them.

Impressed with the differences in chemical behaviour revealed by the enzymes of micro-organisms, Fischer turned attention to secretions of animal origin, and in 1896, assisted by Niebel, studied the attitude of starch, glycogen, maltose, lactose, sucrose, trehalose, amygdalin, and some artificial glucosides towards blood serum from several sources and a great variety of tissue extracts and juices. It was in the domain of proteins and polypeptides, however, that the principal use was made of these agents. In 1903, when his fruitful association with Abderhalden began, casein was subjected to protracted hydrolysis by the pancreatic enzyme, with the surprising result that proline and phenylalanine, although liberated from the protein by acid and alkaline hydrolysis, were not recognisable amongst the products. These were tyrosine, alanine, leucine, glutamic acid, aspartic acid, and a polypeptide material which, when hydrolysed by hydrochloric acid, gave an amount of the two missing amino-acids in close correspondence with the quantity obtainable from casein itself, together with alanine, leucine, glutamic acid, and aspartic acid. It was also found that edestin, hæmoglobin, egg-albumin, fibrin, and serum-globulin resemble casein in the foregoing aspect, and thus was revealed a product of hydrolysis lying between the peptones and the amino-acids.

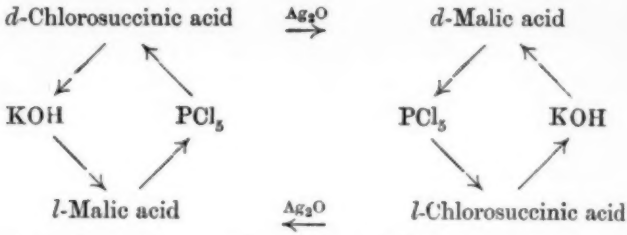
Acceptance of the relationship between proteins and amino-acids, established by the interposition of polypeptides, involves the

susceptibility of these materials to zymolysis, and, as their number grew, Fischer accumulated many studies of such action. Thus with Bergell (1903) he found that under conditions which favour the tryptolysis of naphthalenesulphoglycyl-*l*-tyrosine and carboethoxyglycyl-*dl*-leucine there is no change with glycylglycine, naphthalenesulphoglycyl-*d*-alanine, and hippuric acid; later it was shown that glycyl-*l*-tyrosine and leucylalanine may be tryptolysed, the disruption of the latter resembling that of carboethoxyglycylleucine by giving rise to active products. This branch of inquiry was greatly extended with the assistance of Abderhalden in 1905, when twenty-nine polypeptides were differentiated by their behaviour towards the tryptic enzyme, leading to conclusions based on the number, individuality, and configuration of the amino-acids involved. At the same time, it was found that glycyl-*l*-tyrosine, dialanylcystine, leucylalanine, leucylglycine, and leucylleucine are not hydrolysed by pepsin–hydrochloric acid.

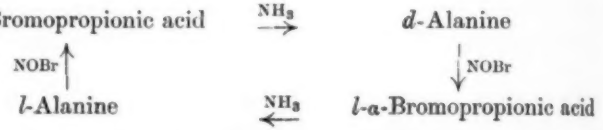
Thereafter, the development of this field has been left to other workers, of whom Abderhalden is recognised as the pioneer, and the remarkable achievements of the subsequent period are a splendid tribute to Fischer's foresight and genius in laying the foundations of a branch of science at once so complex and so fundamental. He it was, indeed, who first clothed with systematic experimental observations and established facts the dictum of Berzelius (1837) "that in living plants and animals there take place thousands of catalytic processes between tissues and fluids."

The Walden Inversion.

Prior to 1895, the conversion of an optically active substance into its enantiomorph had been accomplished only by racemisation preliminary to resolution by one of Pasteur's methods. The system of cyclic changes dating from that year, and classified as the "Walden inversion," exhibited a direct reversal of rotatory power, and offered, perhaps, the most elusive amongst the many interesting problems connected with optical activity. Walden showed that each chlorosuccinic acid will give both malic acids according to the agent selected for replacing halogen by hydroxyl; silver oxide leaves the sign unchanged, whilst potassium hydroxide produces an acid of opposite sign. As the regeneration of chlorosuccinic acid from malic acid by phosphorus pentachloride also involves a change of sign, the typical Walden inversion is represented as follows:



During the years 1907—1911, Fischer described numerous examples of sign-reversal arising from the study of amino-acids, for instance,



In the foregoing cycle it is a matter of indifference whether the replacement of halogen by an amino-group takes place in the acid or in the ester, but the converse change, attended by reversal of sign when alanine is transformed into α-bromopropionic acid, proceeds without reversal when alanine ester is converted into α-bromopropionic ester, the latter yielding, when hydrolysed, an acid having the same sign as the alanine employed. Other amino-acids, such as leucine, aspartic acid and phenylalanine, are distinguished from their esters in the same way, but *l*-valine (α-amino-*iso*valeric acid), whilst giving with nitrosyl bromide *d*-α-bromo*iso*-valeric acid, is regenerated by the action of ammonia on that substance. Fischer found, also, that whilst *l*-lactic acid arises from *l*-α-bromopropionic acid by action of silver oxide, this agent converts *l*-α-bromopropionylglycine into a hydroxy-compound which gives *d*-lactic acid on hydrolysis. Furthermore, although *l*-valine is produced when ammonia acts on *d*-α-bromo*iso*valeric acid, *d*-valine arises from hydrolysing the product of *d*-α-bromo*iso*-valerylglycine and ammonia.

At first it was believed that this type of change is associated only with α-substitution, Fischer and Scheibler showing that the following transformations are free from reversal of configuration:

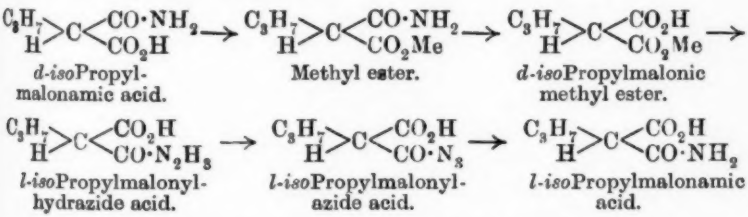
$$l\text{-}\beta\text{-Hydroxybutyric acid} \xrightarrow{PCl_5} \xleftarrow[Ag_2O \text{ or } H_2O]{} d\text{-}\beta\text{-Chlorobutyric acid.}$$

In 1911, however, they found that each β-aminobutyric acid will give both β-hydroxybutyric acids, according to the method of changing the substituents, thus:

$$d\text{-Hydroxyl} \xleftarrow{H_2O} l\text{-Chloro-} \xleftarrow{NOCl} d\text{-Amino-} \xrightarrow{HNO_2} l\text{-Hydroxyl.}$$

The same year witnessed a comprehensive survey of the subject by Fischer (*Annalen*, 1911, **381**, 123), who described an ingenious model in which the central carbon atom and the movable groups have bristle-covered faces to facilitate their attachment in selected positions; thus the four substituents may be moved at the same time over the spherical surface of a central carbon atom, or they may be transferred singly to positions adjacent to those which they previously occupied. He represented substitution as preceded by the formation of an additive compound, which, on disruption, may or may not lead to a relative distribution of the substituents; thus the entrant group need not take the place of the one it dislodges, and if it assumes another position, the configuration of the product will differ from that of the original material. Viewed in this light, the Walden inversion is a normal process determined by the chemical agents employed and by the nature of the other groups attached to the asymmetric carbon atom. Simultaneously, the problem was discussed by Werner from the standpoint of supplemental valency, and criticisms by Biilmann in the following year led to a rejoinder by Fischer; it is not the purpose of this reference, however, to do more than indicate his contact with the subject, which still awaits a complete explanation.

Two important deductions from the theory of the asymmetric carbon atom received experimental confirmation at the hands of Emil Fischer by methods which the Walden inversion cannot vitiate, because the involved groups remain attached to the central nucleus throughout the changes. Assisted by F. Brauns, in 1914 he showed that optical activity disappears when two of the different groups become identical, producing ethyl*iso*propylmalonic acid (inactive) from *d*-ethyl*iso*propylmalonamic acid. He next made the following transformations:



Since the original *d-iso*propylmalonamic acid has $[\alpha]_D$ 48·8°, and the resulting *l*-acid $[\alpha]_D$ −44·4°, agreement is sufficiently close to prove that the expectation of sign-reversal following systematic interchange of two substituents in an asymmetric system has been experimentally realised.

Technology.

Fischer's relationship to the chemical industry was intimate and beneficent. Viewed superficially, the subjects on which is founded his unrivalled reputation as an investigator do not appear to have much bearing on factory problems; but the value of a life-work cannot be estimated with accuracy unless the qualities of the worker are taken into account. It is a common observation that absorption in laboratory practice, coupled with unremitted study and theoretical reflection, tend to draw the chemical investigator so much away from practical affairs as to diminish his perception of commercial and industrial factors. Either because of his early training, or owing to his inborn love of knowledge in all its branches, Fischer was unusually free from this disability, and the reliance placed on his opinions by leaders of the German chemical industry ultimately grew into an attitude of trust which was quite exceptional. As early as 1883 he was a marked man, for in that year the chairman of the Badische factory selected him as director of research, in succession to Caro, at a salary of £5000, but the offer was not accepted. Whilst it is impossible to compute the results which might have accrued from his occupancy of the post, it is equally impossible to regret the decision which he then made. Although so tempting a proposal could not detach him from his chosen course, he remained throughout life in close communion with factory operations, becoming and continuing *persona grata* with the chemical industrial magnates and exerting a profound influence on the industry.

Probably his greatest direct contribution to technology lies in the stream of young chemists passing regularly from his laboratory to the factories, men soundly trained in the methods of systematic inquiry and in whom a love of chemistry had been made fruitful by the radiation of his galvanising personality. Nevertheless, more concrete associations with manufacture emerge from time to time. Phenylhydrazine was destined to become one of these, although its contact with industry through antipyrine, pyramidone, and tartrazine was made by other hands.

As already noticed, it might have been expected that the subject of his thesis for the doctorate, fluorescein, and the important contribution to the structure of triphenylmethane colouring matters for which he and his cousin were responsible so early in life, would have committed him definitively to the chemistry of dyes; but his interest in biochemistry rapidly became absorbingly predominant, and it was consequently in the field of synthetic drugs that his

personal connexion with chemical industry became most fruitful. Based on principles developed in his laboratory, methods were adopted in the Böhringer and Bayer factories for the manufacture of caffeine, theophylline, and theobromine, whilst the practicability of replacing atropine by a synthetical substitute may be traced to his early work on triacetonalkamine.

A very definite contribution to manufacturing practice was made in 1903, when the improvement which he effected in the production of diethylbarbituric acid, arising from his work on purines, led to that substance becoming one of the most valuable hypnotics in pharmacy under the name veronal, the manufacture being undertaken by the Merck, Bayer, and Höchst factories. His collaborator in that work, von Mering, was associated with him also in 1907, when calcium iodobehenate, or sajodin, was brought out as a tasteless preparation of iodine easily tolerated by the organism. This was followed by calcium dibromobehenate, or sabromin, as an instrument for introducing bromine, and the production of both remedies was undertaken by the Bayer and Höchst factories, the latter developing also the preparation of strontium chloroarsinobehenolate, or elarson, in connexion with which the preliminary experiments were made by Fischer and Klemperer. When war broke out he was taking part in the search for a carcinoma remedy, that path so thickly strewn with hopes deferred.

It is not difficult to imagine the demands which were made on his energy and wisdom during the five years which were destined to be the closing period of his life, and these have been delineated by A. von Weinberg. It is now known that the war could not have been continued by Germany beyond the middle of 1915 had not synthetic nitric acid begun to take the place of Chile saltpetre. The probable course of events revealed itself to Fischer in September, 1914, when he urged on the Westphalian manufacturers the need of prompt action, and was rebuked in consequence by the military authorities; but on October 1st he made a detailed report to the War Ministry with reference to the possibility of increasing the supply of ammonia from coke-ovens, and his services were in constant requisition during the growth of the synthetic nitric acid industry, which subsequently reached such enormous proportions.

Two months later the diminishing store of camphor led him to recommend the use of dimethyl- and diethyldiphenylcarbamide in powder stabilisation, these being actually adopted, and in February, 1915, he was presiding over a commission for stimulating the production of benzene and toluene by gas-stripping. Whilst the commission accomplished its original purpose before the end of that year, it remained in being to deal with such matters as the pro-

duction of heavy oil from naphthalene, the extraction of phenol and cresol from coke-oven tar, and, at the beginning of 1916, with a search for applications of the superabundance of benzene which then existed. By the end of that year, however, the Hindenburg programme had shattered the technical scheme for providing a sufficiency of this hydrocarbon, and converted plenty into famine; Fischer then demanded the demobilisation of 50,000 coal-miners.

As early as 1915 his attention was directed to the dwindling of pyrites reserves, and he became president of a gypsum and kieserite commission, charged with inquiry into means for utilising the sulphur content of those minerals; although technical difficulties prevented the application of kieserite to this purpose, the obstacles connected with gypsum were overcome and much valuable information was obtained.

At the beginning of 1916 Germany found it necessary to limit the saponification of fats, and Fischer was invited to examine more closely the alternative sources of glycerol. His first idea being to replace that substance by glycol, he recommended the construction of a factory at Essen for that purpose, but the subsequent process of Connstein and Lüdecke for producing glycerol by fermentation obviated the need for this measure. He took an active part in developing the new industry, in utilising the aldehyde-alcohol which offered itself as a by-product, and in solving the cognate problem of converting fatty acids to service as food, the result of which was ester-margarine.

It was the food shortage in all its aspects, however, which claimed his attention more and more pressingly. Interwoven with the demands of the explosives industry came the call for nitrogen fertilisers, and in January, 1917, associated with Nernst and Haber, he urged on the War Ministry the need for a foodstuffs commission to assume the task of stimulating food production on behalf of men and animals. With terrible earnestness he portrayed the secondary position occupied by patriotic heroism in relation to physiological law, the neglect of which must lead inevitably to psychological breakdown. From that time until its final session in 1918, the commission attacked with feverish energy a multitude of diverse problems, amongst which the conversion of straw into a digestible fodder for horses and cattle took a prominent place. The possibilities of wood, also, were explored from this point of view, the utilisation of leaves, rushes, and couchgrass (quitch), the germination of grain, and the preservation of vegetables. With special attention Fischer devoted himself to providing a coffee substitute, improving considerably on the knowledge which he had accumulated prior to the war, whilst attempts to augment the

supply of albuminoid esculents emerged in "mineral yeast" and the utilisation of lupines.

In spite of all these efforts, however, Fischer and his colleagues foresaw the inevitable results of increased disease, diminished capacity for work, and impaired moral resistance arising from the lamentable condition of the people. They embodied their conclusions in a memorial addressed to the heads of military and civil government in January, 1918, explaining the helplessness of science and technology to meet the situation, but their representations were unheeded.

Conclusion.

Harassed by these distractions and anxieties, tormented from time to time by bodily pain, and bowed down by the loss of his second and third sons, his inextinguishable spirit found refuge in the calm pursuit of scientific inquiry. It was during this period that his life-long work on carbohydrates and the correlation of these with depsides received many decisive additions, and in the closing months of 1918 he witnessed, in the establishment of the "Deutsche Gesellschaft zur Förderung des Chemischen Unterrichts," the launch of an enterprise very near to his heart. As the war continued, he had become gravely concerned at the diversion of young chemists to its requirements, and the consequent injury to the scientific spirit of the new generation. To assist in combating this danger and the accompanying embarrassment to teaching institutions arising from the diminished value of money, he raised a considerable fund, which, in his own words, constituted "der letzte Dienst den ich der deutschen Wissenschaft leisten kann."

In this connexion, it should be remembered also that it was largely by the inspiration and energy of Emil Fischer that the idea of establishing a research foundation independent of teaching duties ultimately took shape in the Kaiser-Wilhelm-Institut für Chemie. Associated with Nernst and Ostwald, he had invited a company, amply representing both science and industry, to discuss preliminaries in October, 1905, but it was not until March, 1908, that the "Verein Chemische Reichsanstalt" was legally registered for the purpose of advancing chemical science and technology. Although a suitable site at Dahlem was allocated by the Prussian Treasury, and many substantial donations had been made, it was not until the projected foundation of the Kaiser-Wilhelm-Gesellschaft in 1910, and the subsequent co-operation of this body with the Verein, that constructive steps could be taken. These culminated in the ceremony witnessed by the German Emperor on October

23rd, 1912, when Fischer, in the name of the Verein Chemische Reichsanstalt, as president of the executive committee, transferred the building to the president of the Kaiser-Wilhelm-Gesellschaft.

His life-work has now been reviewed, but only another generation can grasp its full significance. We shall not survive to witness the momentous consequences of its impulse, but we can perceive that Emil Fischer, in one branch of science the master, gave a new meaning to another branch, physiology, inasmuch as he placed biochemistry on an assured basis. The germ of this profound influence may be traced to a remote inquiry completely detached, as it would then have seemed in the mind of its author, from the trend of its ultimate development. The effect which was destined to be produced on physiological chemistry by the discovery of phenylhydrazine in 1875 offers but another example of the constant interplay between fact and thought. Although twelve years elapsed before that base enabled him to claim the synthesis of a natural sugar, progress thereafter was rapid and sweeping. The array of synthetical carbohydrates which had been assembled by the year 1894 provided him with the material necessary for the fundamental discovery that the specific action of an enzyme is intimately related to the configuration of the substrate. In the wealth of practical achievement which followed this discovery, the applications of its underlying principle constantly recur. The classification of the glucosides was a substantial consequence, but far more important was the utilisation of tissue extracts in the study of artificial polypeptides, showing that it is only those constructed of the amino-acids supplied by nature which yield to the attack of peptoclastic enzymes. Thus it may be claimed for Fischer that he forged and perfected a new and delicate instrument with which the investigator may solve abstruse problems in biochemistry, for when once the technique is acquired, the use of enzymes in configuration diagnosis is unapproached by ordinary chemical processes in respect of precision and rapidity.

Reflecting on the essence of life in its chemical aspect, regarding the act of living as a complex alternation of digestion, assimilation, and oxidation, the mind begins to arrange in one beautiful fabric the coloured strands from which is woven Fischer's contribution to the knowledge of the centuries. He not only regularised the most fruitful of laboratory methods for studying life processes, but he assembled more richly, and in greater variety than any other chemist, the materials on which those processes depend. Carbohydrates, glucosides, depsides, purines, and polypeptides have, during the years of his activity, been brought to our delighted vision and ranged in perspective by his control of enzymes. As

interpreted by him, we recognise amino-acids as the basis of our being. All this knowledge will give definite form to countless inquiries dealing with digestion and assimilation, and by shaping the problems connected with such changes will assist in taking that first and most important step towards solving them. Indeed, it is not unjustifiable to hope that further advances along the lines now firmly laid by his life-work may bring biochemists of a future period to a clearer view of that elusive province in which hormones and advitants (miscalled vitamines) exercise their subtle influence on the alchemy of living bodies.

Even when due allowance has been made for the storehouse of accumulated facts on which the chemists of his era were empowered to draw and for the variety of technique which was at their command, it can scarcely be claimed that in wealth of revelation and manipulative skill Emil Fischer is eclipsed by any of his predecessors. It is difficult to imagine that he can be surpassed by any of his successors; but, whether this be so or not, his achievement will remain for all time a monument of industry, a masterpiece of symmetry and a gospel of inspiration. His contemporaries, who have watched the growth of a wonderful structure with admiration and pride, may leave to posterity, in happy confidence, the office of enshrining his work in the history of their beloved science:

> "For Time shall with his ready pencil stand,
> Retouch your figures with his ripening hand,
> To future ages shall your fame convey
> And give more beauties than he takes away."

CXXXI.—*Studies in Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom. Part III. Resolution of Phenylmethylethylazonium, Phenylbenzylpropylazonium, and Phenylbenzylallylazonium Iodides into Optically Active Components.*

By Bawa Kartar Singh.

In Parts I and II of this series of researches (T., 1913, **103**, 604; 1914, **105**, 1972) the author has described the resolution of two members of a new type of enantiomorphous compounds,

$$R_1R_2R_3XN{\cdot}NH_2,$$

the asymmetry, and consequently the optical activity, of which is associated with the presence of an asymmetric nitrogen atom.

The present investigation, which is a continuation of this work, is concerned with the resolution of phenylmethylethylazonium iodide, the previously determined value of the molecular rotatory power of which was considered to be rather low (*loc. cit.*), in addition to that of two other members, namely, *phenylbenzylpropylazonium* and *phenylbenzylallylazonium iodides*.

Phenylmethylethylazonium iodide was resolved with the aid of silver *d*-α-bromocamphor-β-sulphonate. The *l*B*d*A salt, being less soluble, separated in a crystalline form and gave, for the *l*-basic ion, $[M]_D$ −23°, the maximum rotation of −30° having already been obtained from the hydrogen tartrate (*loc. cit.*). It is thus very probable that the former value of −30° is the maximum molecular rotatory power of the *l*-basic ion.

Another point of interest is that *l*-phenylmethylethylazonium picrate has almost identical values of $[M]_D$ in chloroform and methyl alcohol solutions (see p. 1206), and it thus stands in noteworthy contrast with phenylbenzylmethylazonium picrate, the value of $[M]_D$ of which is three times as high in chloroform as in methyl alcohol (T., 1914, **105**, 1984). This points to molecular association of the latter picrate in chloroform, but, so far, this view has not been corroborated by a determination of molecular weights in the two solvents.

Phenylbenzylpropylazonium iodide could only be obtained in one way, namely, by the action of benzyl iodide on phenylpropylhydrazine. In this reaction, a very small amount of a hydriodide was also formed as a by-product The action of propyl iodide on

phenylbenzylhydrazine gave two hydriodides melting at 146—147° and 162—163° respectively, besides ammonium iodide. No azonium iodide was, however, formed in this reaction. The action of propyl iodide thus seems to be abnormal, and was further studied on two other hydrazines. In the case of phenylmethylhydrazine, the sole product of the action of this iodide was ammonium iodide, and in that of phenylpropylhydrazine at first no product was formed, but on keeping the mixture for some time a very minute quantity of ammonium iodide was isolated. It may be suggested that the secondary hydrazine is slowly reduced to an amine and ammonia, and the latter substance combines with hydriodic acid to form ammonium iodide. The hydriodic acid may be produced from the hydrolytic decomposition of propyl iodide, and it very probably acts also as the reducing agent.

Phenylbenzylallylazonium iodide was prepared from the action of benzyl iodide on phenylallylhydrazine. This reaction was quite normal.

Resolution.—Phenylbenzylpropylazonium iodide was resolved by the aid of silver *d*-camphor-β-sulphonate and *d*-α-bromocamphor-β-sulphonate. In the case of the camphorsulphonates, the *d*B*d*A salt, being less soluble in a mixture of methyl alcohol and ether, first separated out. It has $[M]_D$ +357·5° in methyl alcohol and +300·5° in aqueous solution. The *l*B*d*A salt was obtained by recrystallisation from water, in which it is less soluble than the other component, and has $[M]_D$ −153·2° in methyl alcohol and −190·9° in aqueous solution. Taking $[M]_D$ for the *d*-camphorsulphonic acid ion as +53°, the *d*B*d*A salt gives +247·5° and the *l*B*d*A salt −243·9° for the *d*- and *l*-basic ions in aqueous solution respectively.

On the other hand, if we assume that the salts *d*B*d*A and *l*B*d*A behave normally in respect of the additive character of the molecular rotatory power of the two ions in aqueous solution, the value of $[M]_D$ for the *d*-camphorsulphonic acid ion is deduced to be +54·8°, and that for the basic ion ±245·7° (see p. 1210).

The agreement between the above figures is sufficiently close, and the value of $[M]_D$ for the *d*-camphorsulphonic acid as above deduced further shows that the two salts *d*B*d*A, *l*B*d*A have been obtained in a pure condition.

It has already been pointed out in the case of the camphorsulphonates of phenylbenzylmethylazonium (T., 1914, **105**, 1973) that three cases may occur when an externally compensated base is crystallised with an optically active acid: (1) the two salts *d*B*d*A, *l*B*d*A crystallise separately, so that each may be readily isolated; (2) a partly racemic compound, *d*B*l*B, 2*d*A, may be

formed, in which case resolution is impossible; (3) each crystal which separates may contain both the salts *d*B*d*A, *l*B*d*A in varying proportions; in other words, the two salts form solid solutions, one in the other, and resolution is very slow and incomplete. In the case of the camphorsulphonates of phenylbenzylpropylazonium, behaviour of two kinds (types 1 and 3) is observed. After some of the *d*B*d*A, *l*B*d*A salts are separated in a pure condition, the residual salt, having $[M]_D$ about $+35°$, consists of 46 per cent. of the *d*B*d*A and 54 per cent. of the *l*B*d*A component. On further crystallisation from water, as well as from a mixture of methyl alcohol and ether, resolution proceeds extremely slowly, as is seen from the rotation constants. It is thus clear that the two salts have formed solid solutions, one in the other, when their composition corresponds with 46 per cent. of the *d*B*d*A and 54 per cent. of the *l*B*d*A component.

In the case of the bromocamphorsulphonates, the *l*B*d*A component, which melts at a higher temperature, first crystallises from a mixture of methyl alcohol and ether. The *d*B*d*A component, on recrystallisation, is obtained as an oil, which could not be solidified. The pure *l*B*d*A salt melts at 178—179°, and has $[M]_D$ $+71·2°$ in aqueous solution.

Phenylbenzylallylazonium iodide was resolved with the aid of silver *d*-camphor-*β*-sulphonate. The *d*B*d*A component, being less soluble in methyl alcohol, first separated out. It melts at 147—148°, and has $[M]_D$ $+190·3°$ in aqueous solution, $+265°$ in chloroform solution, $+285·7°$ in methyl alcohol, and $+319·2°$ in ethyl alcohol.

Experimental.

Phenylmethylethylazonium d-*α*-*Bromocamphor*-*β*-*sulphonate*, $PhMeEt(NH_2)N·SO_3·C_{10}H_{14}OBr$.

Finely powdered azonium iodide (25 grams) was added in small quantities at a time to one molecular proportion of silver *d*-*α*-bromocamphor-*β*-sulphonate (37·6 grams) dissolved in boiling methyl alcohol on the water-bath. The contents of the flask were kept shaken, and, after the addition of the whole of the azonium iodide, the heating was continued for half an hour to complete the reaction. The methyl alcohol was distilled off, and the residue, consisting of solid silver iodide and the syrupy bromocamphorsulphonate, was extracted in the usual way with methyl alcohol. On evaporating the methyl alcohol, an oily residue remained, which did not crystallise even on keeping for six days. It was again dissolved in alcohol, and precipitated as an oil by the addition of ether. After some time fine, needle-shaped crystals began to

appear, and a portion of the oil slowly became crystalline; this amounted to 9·7 grams and melted at 152—153°. The remaining portion of the oil did not crystallise even on keeping under ether for six months (Found: C = 49·05; H = 6·74. $C_{19}H_{29}O_4N_2Br$ requires C = 49·46; H = 6·29 per cent.).

The rotatory power* of the salt was determined at 29° in aqueous solution:

Substance. Gram.	Time.	α_D.	$[M]_D$.
0·1738	—	+1·11°	+293·0°
0·1738	After 25 hours.	1·13	298·3

The above camphorsulphonate (8·8 grams) was dissolved in the least possible quantity of methyl alcohol and precipitated by gradual addition of ether, with the following result:

Fraction.	Yield. Grams.	M. p.	Substance. Gram.	α_D.	$[M]_D$.
A.....	2·2	154—155°	0·2960	+1·86°	+288·3°
B.....	5·9	155	0·1792 (in 20 c.c.)	1·12	286·6

Fraction *B* was submitted to the same process, and the rotatory power of fractions *C* and *D* into which it was resolved was determined, with the following result:

Fraction.	Yield. Grams.	M. p.	Substance. Gram.	α_D.	$[M]_D$.
C	2·1	155—156°	0·2184	+1·41°	+296·2°
D	3·0	154—155	0·2454	1·54	287·8

The rotatory power in all the above cases was determined in water at 29—30°. The lowest value of $[M]_D$ for the *l*B*d*A salt is about +287°, and since $[M]_D$ for silver *d*-α-bromocamphor-β-sulphonate (Pope and Read, T., 1914, **105**, 809) is +310°, the molecular rotatory power for the *l*-phenylmethylethylazonium ion is −23° (287—310).

dl-*Phenylmethylethylazonium Picrate*, $PhMeEt(NH_2)N{\cdot}O{\cdot}C_6H_2O_6N_3$.

This salt was obtained from the racemic azonium iodide in the usual way as yellow prisms melting at 110—111°. It is very readily soluble in acetone, less so in methyl alcohol, ethyl alcohol, or chloroform, moderately so in water, and insoluble in ether (Found: N = 18·63. $C_{15}H_{17}O_7N_5$ requires N = 18·47 per cent.).

* The given weight of the substance was dissolved in 19·9 c.c. of solvent, and the rotatory power determination was made in a 2-dcm. tube about thirty minutes after solution. This applies to all the observations recorded in this paper, unless the contrary is stated.

l-Phenylmethylethylazonium Picrate.

The active picrate was prepared by adding an alcoholic solution of the bromocamphorsulphonate of the *l*-base to an alcoholic solution of picric acid. On concentrating in the cold, water was added, when yellow prisms separated, which, after one or more recrystallisations from alcohol and ether, melted and decomposed at 114—115°. A mixture of the *dl*- and *l*-picrate melted at 107—108°. It is very readily soluble in acetone, less so in methyl alcohol, ethyl alcohol, or chloroform, moderately so in water, and insoluble in ether (Found: N = 18·14. $C_{15}H_{17}O_7N_5$ requires N = 18·47 per cent.).

The rotatory-power determinations gave the following values:

Substance. Gram.	Time.	Temperature.	α_D.	$[M]_D$.
0·2748 (in 20 c.c. methyl alcohol)	½ hr.	27·5°	−0·16°	−22·06°
	5 hrs.	27·0	0·17	23·4
0·2977 (in chloroform).....	—	27·0	0·186	23·56
	2¾ hrs.	27·0	0·18	22·08
	7½ ,,	28·0	0·17	21·51
	32 ,,	27·0	0·10	12·67

The rotatory power of the above picrate is practically identical in both the solvents. This is noteworthy, as phenylbenzylmethylazonium picrate has $[M]_D$ three times as high in chloroform as in methyl alcohol (T., 1914, **105**, 1984). This is probably due to association of the molecules of the latter picrate in chloroform.

as-*Phenyl-α-propylhydrazine*, $PhPr^{\alpha}N{\cdot}NH_2$.

This was prepared by dissolving sodium, first obtained in a fine, granular condition, by melting it under xylene and vigorous shaking during cooling, in the calculated quantity of phenylhydrazine at 180°, under diminished pressure, and treating the resulting sodium phenylhydrazine with propyl bromide (Michaelis, *Ber.*, 1897, **30**, 2815). The secondary hydrazine was purified by conversion into its hydrochloride (silky needles), which melts at 147°, and not at 135°, as stated by Michaelis (Found: Cl = 18·89. Calc.: Cl = 19·57 per cent.).

Phenyl-α-propylhydrazine hydroferrocyanide,

$$(PhPr^{\alpha}N{\cdot}NH_2)_2H_4Fe(CN)_6,$$

is obtained as a white precipitate by the addition of a concentrated solution of potassium ferrocyanide to a concentrated solution of phenylpropylhydrazine hydrochloride acidified with hydrochloric acid. It is successively washed with a little water, alcohol, and ether, and dried in a vacuum desiccator. It is very readily soluble

in water, but less so in alcohol. On exposing it to the air for some time, it acquires a violet-blue colour (Found: Fe=10·67; N=26·65. $(C_9H_{14}N_2)_2H_4Fe(CN)_6$ requires Fe=10·85; N=27·14 per cent.).

dl-*Phenylbenzylpropylazonium Iodide*, $PhPr^{n}(CH_2Ph)(NH_2)NI$.

(*a*) *By the Action of Benzyl Iodide on Phenylpropylhydrazine.*—An ice-cold ethereal solution of phenylpropylhydrazine (from 30 grams of the hydrochloride) was added to one molecular proportion of an ethereal solution of benzyl iodide, also cooled in ice. The crude product (33·5 grams), after recrystallisation from methyl alcohol and ether, melted and decomposed at 125—126°. In some experiments, the yield was even better. It is very readily soluble in methyl alcohol, somewhat less so in ethyl alcohol, still less so in water, and insoluble in benzene or ether (Found: I=34·61. $C_{16}H_{21}N_2I$ requires I=34·49 per cent.).

From the filtrate, on keeping for some time, a very small amount of another substance separated. This was not an azonium iodide, but a hydriodide, as it gave an oil on treatment with a solution of sodium carbonate.

(*b*) *The Action of Propyl Iodide on Phenylbenzylhydrazine.*—The action of propyl iodide on phenylbenzylhydrazine did not give the azonium iodide obtained under (*a*), but what appeared to be a hydriodide, as the product gave an oil on treatment with sodium carbonate. The mother liquor, on keeping for several weeks, deposited a small amount of another substance which did not melt, but evolved ammonia with potassium hydroxide. It appeared to be ammonium iodide (Found: I=86·88. Calc.: I=87·6 per cent.).

dl-*Phenylbenzylpropylazonium chloride*,

$$PhPr^{n}(CH_2Ph)(NH_2)NCl,$$

is obtained in the usual way from the corresponding azonium iodide, and crystallises from alcohol and ether in colourless prisms melting and decomposing at 145—146°. It is very readily soluble in methyl alcohol, ethyl alcohol, acetone, or water, but insoluble in ether (Found: N=10·53. $C_{16}H_{21}N_2Cl$ requires N=10·15 per cent.).

The corresponding *platinichloride* is a buff-coloured substance melting and decomposing at 151°. It is insoluble in water or organic media (Found: Pt=22·03. $(C_{16}H_{21}N_2Cl)_2PtCl_4$ requires Pt=21·93 per cent.).

The dl-*aurichloride* is first obtained as an oil, which, on rubbing and allowing to remain, becomes crystalline. It recrystallises from

hot alcohol in yellow prisms melting and decomposing at 132—133°. It is very readily soluble in acetone, sparingly so in methyl alcohol, ethyl alcohol, or chloroform, and insoluble in water or ether (Found: Au = 34·08. $C_{16}H_{21}N_2Cl,AuCl_3$ requires Au = 34·0 per cent.).

On keeping for a few days in a stoppered bottle, it decomposes to a dark brown, semi-solid mass, hydrogen chloride being evolved.

Phenylbenzylpropylazonium d-*Camphor-β-sulphonate*, $PhPr^{\alpha}(CH_2Ph)(NH_2)N{\cdot}SO_3{\cdot}C_{10}H_{15}O$.

Finely powdered phenylbenzylpropylazonium iodide (30 grams) was added in small quantities at a time to one molecular proportion of silver *d*-camphor-β-sulphonate contained in a mortar. Methyl alcohol, containing a few drops of water, was added to moisten the contents of the mortar, and the mixture was carefully triturated. This procedure was adopted in place of the usual one in order to diminish the decomposition which resulted when the constituents were heated together with ethyl acetate or alcohol. The mortar was kept in a vacuum desiccator, and the solid residue was extracted with methyl alcohol in a Soxhlet apparatus. On evaporating off the alcohol, 33·8 grams of the camphorsulphonate (theoretical yield, 38·4 grams) melting at 185° were obtained. It is very readily soluble in methyl alcohol, ethyl alcohol, acetone, or chloroform, moderately so in water, and insoluble in benzene or ether (Found: C = 65·88; H = 7·63. $C_{26}H_{36}O_4N_2S$ requires C = 66·12; H = 7·63 per cent.).

d-*Phenylbenzylpropylazonium* d-*Camphor-β-sulphonate*.

The camphorsulphonate (32·8 grams), as prepared above, was subjected to fractional precipitation by first dissolving it in the least possible quantity of methyl alcohol, and then gradually adding pure anhydrous ether. The following five fractions were obtained:

Fraction.	Yield. Grams.	M. p.	Substance. Gram.	α_D.	$[M]_D$.
1	6·9	187°	0·1727	+0·76°	+206·7°
2	6·8	190—191	0·1858	0·145	36·65
3	16·7	189	0·1965	0·32	76·47
4	0·33	186	0·1982	0·307	72·75
5	1·7	184	0·1806	0·24	62·41

The rotatory power was determined in methyl alcohol at 30—31°. Fraction 1, after recrystallising several times, gave the pure *dBdA* salt melting at 190°, with the following values for rotatory power:

Solvent.	Temperature.	Time. Hours.	Substance. Gram.	α_D.	$[M]_D$.
Methyl alcohol	24·0°	—	0·1340	+1·02°	+357·5°
Water	27·0	—	0·0963	0·616	300·5
„	25·5	23	0·0963	0·613	299·0
„	26·0	47	0·0963	0·61	297·5

Thus the pure salt, *d*B*d*A, melts at 190°, and has $[M]_D$ +357·5° in methyl alcohol and +300·5° in aqueous solution.

l-Phenylbenzylpropylazonium d-*Camphor-β-sulphonate.*

Fractions 2 and 3 (amounting to 23·5 grams), after several further fractionations in the usual way, gave 6 grams of salt melting at 189°, which was optically inactive. The resolution in this way, however, proceeded very slowly, and as a preliminary experiment showed that the *l*B*d*A salt is less soluble in water, the optically inactive fraction was recrystallised from that solvent.

Fraction.	Yield. Grams.	M. p.	Substance. Gram.	α_D.	$[M]_D$.
*a*1.....	2·0	188°	0·2280	−0·45°	− 92·69°
*a*2.....	3·6	186	0·2073	+0·26	+ 58·92
Fraction *a*1 was twice again recrystallised from hot water:					
*a*3.....	0·55	190	0·1202	−0·485	−189·5
*a*4.....	0·2	189	0·1836	−0·64	−164·5
Fraction *a*3 similarly gave fractions *a*5 and *a*6:					
*a*5.....	0·26	191	0·1459	−0·59	−190·9
After 20 hours:			0·1459	−0·58	−187·6
*a*6.....	0·18	—	0·1317	−0·51	−181·9
After 23 hours:				−0·47	−167·6

The rotatory power in the above cases was determined in water at 26—28°.

The rotatory power of fraction *a*5 was also determined in methyl alcohol:

Substance. Gram.	Temperature.	Time. Hours.	α_D.	$[M]_D$.
0·1159	25·5°	—	−0·373°	−151·1°
0·1159	26·0	24	−0·378	−153·2

Thus the pure salt, *l*B*d*A, melts at 191°, and has $[M]_D$ −190·9° in aqueous solution and −151° in methyl alcohol (Found: N=5·81. $C_{26}H_{36}O_4N_2S$ requires N=5·93 per cent.).

After the pure salts, *d*B*d*A and *l*B*d*A, were isolated, there still remained about 15·6 grams of the substance with $[M]_D$ ranging from +29° to +72°. It was repeatedly crystallised, first from water and then from methyl alcohol and ether. Ultimately a salt with $[M]_D$ +35° was obtained, when the rotatory power could

not be changed any further. It thus appears from the slow resolution that the two salts *d*B*d*A, *l*B*d*A have formed a solid solution one in the other. The rotation constants indicate that this fraction consists of about 46 per cent. of the *d*B*d*A and 54 per cent. of the *l*B*d*A salt.

The Molecular Rotatory Powers of the Optically Active Ions in Aqueous Solution from that of the Camphorsulphonates.

The molecular rotatory powers of the two camphorsulphonates, *d*A*d*B and *d*A*l*B, in less than 1 per cent. aqueous solution are tabulated below:

	M. p.	$[M]_D$.
(1) *d*B*d*A	190°	+300·5°
(2) *l*B*d*A	191	−190·9

The algebraical sum of the molecular rotatory powers of these two salts in aqueous solution should be equal to twice the molecular rotatory power of the acid ion, and the algebraical difference should be equal to twice that of the basic ion. The value of $[M]_D$ for the camphorsulphonic acid ion becomes 54·8°, and that for the phenylbenzylpropylazonium ion 245·7°. The agreement between the value of $[M]_D$ for the camphorsulphonic acid ion as deduced above, and that obtained directly, as in the following table, is fairly close:

Temperature.	$[M]_D$.	
20°	51·4°	(Graham, T., 1913, **103**, 764).
20	51·6	(Thomas and Jones,
30	53·6	T., 1906, **89**, 284).

Phenylbenzylpropylazonium d-*α-Bromocamphor-β-sulphonate*, $PhPr^{\alpha}(CH_2Ph)(NH_2)N{\cdot}SO_3{\cdot}C_{10}H_{14}OBr$.

This salt was prepared by the gradual addition of finely powdered azonium iodide (36·1 grams) to one molecular proportion of silver *d*-*α*-bromocamphor-*β*-sulphonate dissolved in hot methyl alcohol. The heating was continued for half an hour on the water-bath under reflux. On filtering off the silver iodide and concentrating the methyl-alcoholic extract on the water-bath, an oil was obtained which at first did not crystallise. It was kept under ether overnight, when it solidified to colourless prisms (41·2 grams) melting at 144—148°. The compound is very readily soluble in methyl alcohol, less so in ethyl alcohol, acetone, or ethyl acetate, sparingly so in water, and insoluble in ether (Found: C=57·22; H=6·62; N=5·27. $C_{26}H_{35}O_4N_2BrS$ requires C=56·63; H=6·35; N=5·08 per cent.).

l-*Phenylbenzylpropylazonium* d-*α-Bromocamphor-β-sulphonate.*

The crude bromocamphorsulphonate (40·2 grams) melting at 144—148°, as obtained in the above way, was subjected to fractional crystallisation, as follows. It was dissolved in the least possible quantity of methyl alcohol and precipitated by gradual addition of ether. In several cases an oil separated, which increased the difficulty of resolution:

Fraction.	Yield. Grams.	M. p.	Substance. Grams.	α_D.	$[M]_D$.
1	12·5	155—156°	0·1087	+0·54°	+272·0°
2	2·3	150—154	0·1193	0·68	312·2
Fraction 1 similarly gave:					
3	3·2	178	0·1183	0·15	69·44
4	5·7	156—158	0·1362	0·742	298·4
Fraction 3, after several more recrystallisations, gave:					
5	1·0	178—179	0·1792	0·22	67·31
		After 8 hours:		0·22	67·31
		After 23½ hours:		0·20	61·1

The rotatory-power determinations in the above cases were made in methyl alcohol at 30—32°. The rotatory power was also determined in aqueous solution in the case of fraction 5:

Substance. Gram.	α_D.	$[M]_D$.
0·0693	+0·09°	+71·2°

Thus the pure *l*B*d*A salt melts at 178—179°, and has $[M]_D$ +71·2° in aqueous solution and +67·3° in methyl alcohol (Found: N=5·13. $C_{26}H_{35}O_4N_2BrS$ requires N=5·08 per cent.).

dl-*Phenylmethylpropylazonium Iodide*, $PhMePr^{\alpha}(NH_2)NI$.

(*a*) *By the Action of Methyl Iodide on* as-*Phenylpropylhydrazine.*—Methyl iodide (6 grams) was added to one molecular proportion of *as*-phenylpropylhydrazine (6 grams) dissolved in ether. Within a short time, the mixture began to deposit a gummy mass, which, on keeping overnight, became crystalline. The crude substance (3·8 grams), after recrystallisation from alcohol and ether, separated in colourless prisms melting and decomposing at 106—107°. It is soluble in methyl alcohol, ethyl alcohol, or water, but insoluble in benzene or ether (Found: I=43·26. $C_{10}H_{17}N_2I$ requires I=43·48 per cent.).

(*b*) *Action of Propyl Iodide on* as-*Phenylmethylhydrazine.*—In

this reaction, the corresponding azonium iodide could not be obtained, but ammonium iodide was isolated (Found: I=87·87. Calc.: I=87·6 per cent.).

Action of Propyl Iodide on as-*Phenylpropylhydrazine.*—In this reaction, also, the corresponding azonium compound (namely, phenyldipropylazonium iodide) could not be obtained, but a small quantity of ammonium iodide was isolated.

dl-*Phenylethylallylazonium Iodide*, $PhEt(C_3H_5)(NH_2)NI$.

Allyl iodide (5 grams) was added to one molecular proportion of *as*-phenylethylhydrazine dissolved in ether and cooled in ice. The mixture was kept overnight, when a gummy substance was deposited, which, however, solidified on rubbing. The crude product (2·4 grams), on recrystallisation from alcohol and ether, separated in colourless prisms melting and decomposing at 107—108°. The salt acquires a violet colour at about 100° (Found: I=42·09. $C_{11}H_{17}N_2I$ requires I=41·78 per cent.).

The corresponding *platinichloride* is obtained, in the usual way, as a pale orange precipitate, consisting of prismatic needles melting and decomposing at 151°. It is very sparingly soluble in cold methyl alcohol, but more readily so in hot, and insoluble in water, acetone, ethyl alcohol, benzene, or ether (Found: Pt=25·71. $(C_{11}H_{17}N_2Cl)_2PtCl_4$ requires Pt=25·62 per cent.).

as-*Phenylallylhydrazine*, $Ph(C_3H_5)N{\cdot}NH_2$.

This is prepared in the usual way by dissolving sodium in a finely divided, granular condition in phenylhydrazine, and treating the resulting sodium phenylhydrazine with allyl bromide (Michaelis and Claessen, *Ber.*, 1889, **22**, 2234). The secondary hydrazine is, however, best purified by leading hydrogen chloride into a chloroform solution of the base. *as*-Phenylallylhydrazine hydrochloride melts at 149—150°, and not at 137°, as stated by Michaelis and Claessen (*loc. cit.*) (Found: Cl=19·76. Calc.: Cl=19·22 per cent.).

dl-*Phenylbenzylallylazonium Iodide*, $Ph(CH_2Ph)(C_3H_5)(NH_2)NI$.

An ice-cold ethereal solution of *as*-phenylallylhydrazine (19·5 grams) was added to one molecular proportion of benzyl iodide (36·0 grams), also cooled in ice. Within a short time, colourless prisms began to deposit. The mixture was kept overnight, and

the crude substance (27·5 grams) melted and decomposed at 115—116°. On recrystallisation from hot alcohol, the temperature of decomposition was raised to 116—117°. The substance is very readily soluble in methyl alcohol, less so in ethyl alcohol, very sparingly so in water or benzene, and insoluble in ether (Found: I=34·89. $C_{16}H_{19}N_2I$ requires I=34·67 per cent.).

Phenylbenzylallylazonium d-*Camphor-β-sulphonate*, $Ph(CH_2Ph)(C_3H_5)(NH_2)N\cdot SO_3\cdot C_{10}H_{15}O$.

Finely powdered azonium iodide (23 grams) was added in small quantities at a time to one molecular proportion of silver *d*-camphor-β-sulphonate contained in a mortar. The mixture was triturated thoroughly in the presence of a little methyl alcohol in the cold, in order to ensure complete double decomposition. It was repeatedly extracted with methyl alcohol, and, on evaporating the solvent by blowing air through the mixture, 18·1 grams of the camphorsulphonate (theoretical yield, 29·6 grams) were obtained. It is very readily soluble in methyl alcohol, ethyl alcohol, or acetone, less so in ethyl acetate or water, sparingly so in benzene, and insoluble in ether.

d-*Phenylbenzylallylazonium* d-*Camphor-β-sulphonate*.

The crude camphorsulphonate (24·3 grams), as obtained in the above way, was subjected to fractional crystallisation from methyl alcohol and ether. The pure salt, *d*B*d*A, melting at 147—148° and having a constant rotatory power, was obtained with great ease. As the rotatory power of this salt varies considerably with the nature of the solvent, the effect of this was studied on the fraction of constant rotatory power:

Solvent.	Time.	Substance. Gram.	α_D.	$[M]_D$.
Ethyl alcohol	—	0·1143	+0·78°	+319·2°
,,	After 5¼ hours.	—	0·74	302·8
,,	,, 22 ,,	—	0·72	294·6
,,	,, 51½ ,,	—	0·62	253·8
Methyl alcohol.....	—	0·0645	0·394	285·7
,,	,, 21½ ,,	—	0·35	253·38
,,	,, 96 ,, (Solution slightly coloured.)	—	0·30	217·5
Chloroform	—	0·0971	0·55	265·0
,,	After 23 hours	—	0·53	255·3
,,	,, 47 ,,	—	0·51	245·7
Water	—	0·0983	0·40	190·3

As the aqueous solution became turbid on keeping, no further readings could be taken. The mean temperature of all the above

observations was 27—29°. There is a marked mutarotation in the case of methyl alcohol and ethyl alcohol, but it is much less in the case of chloroform (Found: N = 6·28. $C_{26}H_{34}O_4N_2S$ requires N = 5·96 per cent.).

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CXXXII.—*The Preparation and Characterisation of Ethylenebromohydrin.*

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ACCORDING to the somewhat scanty references available in the literature, it appears that ethylenebromohydrin has hitherto been prepared only in an impure condition. This remarkable fact in the case of so simple a substance is to be attributed not so much to instability as to the nature of the preparative methods adopted Thus, in the older methods ethylene glycol was utilised as the starting point, the second reagent being either ethylene dibromide (Lourenço, *Ann. Chim. Phys.*, 1863, [iii], **67**, 275), hydrogen bromide (Henry, *Jahresber.*, 1872, 304), or phosphorus tribromide (Demole, *Ber.*, 1876, **9**, 48); whereas, more recently, application has been made of the interaction of ethyleneiodohydrin and bromine (Henry, *ibid.*, 1889, 1321), and the direct addition of hypobromous acid to ethylene (Mokievski, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 900). Of the principles involved in these methods the last is undoubtedly to be preferred, as least liable to give rise to impurities in the resultant ethylenebromohydrin, and the advance which has lately been made in the experimental application of this principle (Read and Williams, T., 1917, **111**, 240; this vol., p. 359) has now enabled us to undertake the preparation of pure ethylenebromohydrin in quantity. At the same time, further study has been directed to the course of the reaction between ethylene and dilute bromine water, the investigation being facilitated by the observation that, as anticipated, the amount of bromohydrin formed during definite intervals may be estimated with sufficient accuracy by a titrimetric determination of the accompanying hydrogen bromide, produced in accordance with the following scheme:

$$\begin{array}{ccccc} HOH & + & Br_2 & \rightleftharpoons & HOBr + HBr \\ & & \downarrow & & \downarrow \\ & & C_2H_4Br_2 & & C_2H_4Br\cdot OH \end{array}$$

The results indicate a remarkable preponderance of bromohydrin in the initial stages of the reaction; thus, when the concentration of bromohydrin has reached 0·2*N* the molecular ratio of ethylenebromohydrin to ethylene dibromide is about 10:1, and in more dilute solutions the value is still higher.

The characteristics of the pure ethylenebromohydrin now obtained differ markedly from the data recorded by previous observers, the density at 20°, for instance, being 1·7629, as compared with the value 1·7195 at 18·6°, given by Henry (*loc. cit.*). In view of the specific interest of this substance as a simple derivative of ethyl alcohol and of its general potentialities as a synthetic agent, it seemed important to establish its main physical and chemical characteristics, and the present paper records some of the results of inquiries directed towards these ends.

Experimental.

Preparation of Pure Ethylenebromohydrin.

Bromine vapour and ethylene were passed into 1500 c.c. of distilled water under the conditions described previously (T., 1920, 117, 359), the operation being continued for several days, until 450 grams of bromine had reacted. The rate of absorption of the bromine, which was slow at first, increased appreciably as the reaction progressed. Ultimately the liquid was neutralised in the cold by the addition of solid sodium carbonate, and the aqueous layer was separated from ethylene dibromide. The latter, of which nearly half the total yield had volatilised in the course of the experiment, was shaken once with water in order to extract dissolved bromohydrin, and dried over calcium chloride; the yield amounted to 80 grams. The amount of hydrogen bromide produced in the reaction, estimated by titration with standard silver nitrate solution, corresponded with 35 per cent. of the bromine added, and thus indicated a 70 per cent. yield of ethylenebromohydrin. In order to allow of the eventual recovery of the bromine present as bromide, the aqueous solution was saturated at the ordinary temperature with anhydrous sodium sulphate rather than with sodium chloride or calcium chloride. Extraction of the bromohydrin was accomplished with three successive quantities of 250 c.c. of ether, and after drying over anhydrous sodium sulphate the ether was expelled on the water-bath.

Repeated distillation of the residual crude ethylenebromohydrin (180 grams) under atmospheric pressure demonstrated the impracticability of effecting an adequate purification by such a method.

The results were, however, of interest as throwing some light upon the varying boiling points, ranging from 147° to 155°, recorded for this substance by earlier investigators. On distillation, the temperature rose gradually to 145°, and the bulk of the liquid distilled between 145° and 150°, although distillation was incomplete even at 155°. The distillates were pale yellow and the residue dark brown, and an appreciable amount of hydrogen bromide was produced during the distillation. After several redistillations the purest material obtained in this way distilled between 146° and 150° (n_D^{20} 1·4925; D_4^{25} 1·7655, vacuum standard). On dilution with water to 60 per cent. strength a slight opalescence appeared, whilst at 50 per cent. a distinct second phase collected, and this persisted on further dilution. The second phase at 35 per cent. had n_D^{20} 1·496, and was shown to contain ethylene dibromide. The purest ethylenebromohydrin obtainable by this method thus contains both ethylene dibromide and hydrogen bromide, as well as traces of water.

By conducting the distillation of the crude ethylenebromohydrin under diminished pressure, however, these impurities are readily eliminated. After the original removal of the ether, a little pure sodium carbonate is added, if necessary, to correct any acidity, and on distilling under diminished pressure a sharp delimitation occurs between the portion of low boiling point and the main fraction. In three different preparations the latter boiled smoothly and constantly at 53·5°/14 mm., 54·5°/14 mm., and 48·5°/13 mm. respectively, and no colour was developed during the distillation. The pure substance is neutral to litmus, and gives no opalescence when diluted with water or silver nitrate solution. As a rule, one distillation under diminished pressure yields a product conforming to these criteria, but sometimes a second distillation is necessary. The average primary yield of pure ethylenebromohydrin obtainable from 450 grams of bromine, in the manner outlined above, is about 120 grams, and further quantities may be extracted from the distillate of low boiling point and the original aqueous liquid. It may be mentioned that the extraction with ether from the aqueous solution is rendered more complete by previously saturating it with sodium sulphate at about 30° instead of at the ordinary temperature. Under such conditions a second phase, consisting mainly of ethylenebromohydrin, separates from the solution concerned, that is, from an approximately 1·2*N*-solution of ethylenebromohydrin containing also sodium bromide. This observation is in conformity with Gomberg's experience with aqueous solutions of ethylenechlorohydrin (*J. Amer. Chem. Soc.*, 1919, **41**, 1426). The volume of ethylene required in practice for this preparation amounts, accord-

ing to our experience, to between twice and thrice the calculated quantity.

Conditions affecting the Course of the Reaction between Ethylene and Dilute Bromine Water.

The effect upon the course of the reaction utilised in the foregoing preparation of certain factors which may be subjected to variation has been discussed in former communications (*loc. cit.*); supplementary work of a quantitative nature has now been carried out in three directions in order to establish the influence upon this process of (1) concentration of the reaction-products, (2) temperature, and (3) light.

(1) For the purpose of ascertaining accurately the amounts of ethylenebromohydrin produced at various stages of the reaction, the determination, from time to time, of hydrogen bromide in an aliquot part of the reaction mixture proved to be satisfactory. In a control experiment, bromine vapour was passed into 500 c.c. of water under the usual conditions, the current of ethylene being replaced by one of air; after an interval of seven hours, during which a pale yellow tint had been maintained in the liquid, the volume of $N/10$-silver nitrate solution required by 5 c.c. was less than one drop, showing that no measurable decomposition of hypobromous acid into hydrogen bromide and oxygen had taken place under the conditions adopted.

In the succeeding preparations of ethylenebromohydrin the customary procedure was observed, except that the bromine was introduced in stages, the amount used being determined in each case by direct weighing. At the end of each stage the liquid was stirred for ten minutes after it had become colourless, and 5 c.c. of the liquid was then withdrawn and titrated with standard silver nitrate solution. Some of the results of two independent series of experiments are tabulated below. The calculations take into account the changes in volume which occur throughout the process, but it was considered unnecessary to apply a correction for the slight loss of bromine by diffusion. The original volumes of water used were 530 c.c. and 550 c.c. respectively, and in the second series a higher final concentration was attained than in the first series. The two sets of results are instructive as illustrating the order of the numerical discrepancies which may occur in determinations of this kind. It should be added that the temperature of the solution, which was ice-cooled, varied from about 7° to 9°, and that the experiments were conducted in diffused daylight.

Stage.	Total bromine present (grams).	Total bromine present as $C_2H_4Br{\cdot}OH$ +HBr (grams).	Percentage of total bromine reacting to form $C_2H_4Br{\cdot}OH$ +HBr.	Concentration of ethylenebromohydrin. Grams per litre.	Concentration of ethylenebromohydrin. Normality.
			Series I.		
1	4·26	4·05	95·1	5·9	0·048
2	12·95	11·85	91·5	17·5	0·140
5	52·56	44·02	83·8	65·0	0·520
8	100·66	76·73	76·2	112·4	0·899
12	160·44	111·00	69·2	161·8	1·294
			Series II.		
1	4·00	3·77	94·3	5·3	0·043
2	12·10	11·09	91·7	15·8	0·126
4	51·36	43·26	84·2	61·7	0·494
7	97·67	75·06	76·9	106·6	0·853
10	167·90	111·29	70·5	156·9	1·255
15	230·41	148·31	64·4	207·6	1·661

These data show that the relative velocity of reaction between bromine and ethylene and hypobromous acid and ethylene respectively is displaced to the advantage of the former reaction as the products accumulate, a result which is probably connected with the great difference in solubility of ethylene dibromide and ethylenebromohydrin, and the separation of the dibromide as a distinct phase. Notwithstanding the change which has just been noted, the molecular ratio of bromohydrin to dibromide (which in the first stage was about 20 : 1) remained greater than unity throughout the range of concentrations investigated.

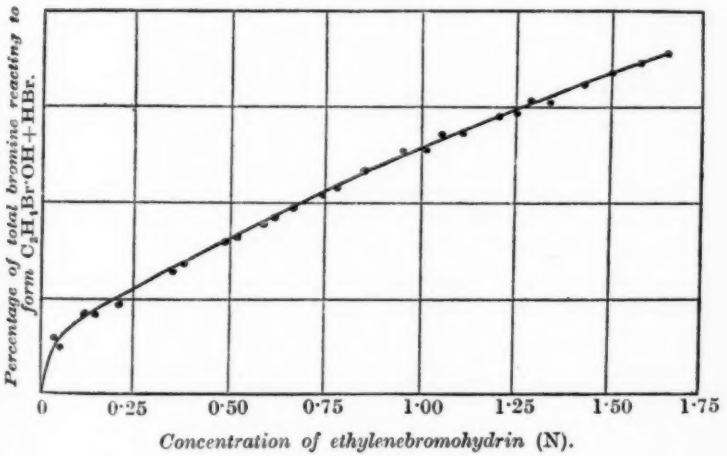
By plotting concentrations of ethylenebromohydrin in terms of normality factor (x) against the corresponding percentages (y) of bromine reacting to form ethylenebromohydrin and hydrogen bromide a regular curve is obtained (Fig. 1), the major portion of which is closely defined by two linear equations, namely, (i) $y = 94{\cdot}37 - 20{\cdot}48x$, and (ii) $y = 89{\cdot}99 - 15{\cdot}47x$. These equations embrace, respectively, the portions of the curve corresponding with (i) $x = 0{\cdot}125$ to $0{\cdot}853$, and (ii) $x = 0{\cdot}853$ to $1{\cdot}661$. The approximate yield of ethylenebromohydrin obtainable from a given amount of bromine, over this range of concentrations, is thus capable of ready calculation.

Attention was also directed to the rate of absorption of the bromine in these experiments; this was found, on the whole, to increase with the concentration of the solution, although irregularities were noticed. Twenty-one successive portions of 8 grams of

bromine took the following respective times, expressed in hours, for complete absorption when introduced with ethylene under the usual conditions into a volume of water originally measuring 530 c.c.: 1·9, 1·6, 1·6, 1·1, 1·1, 1·1, 1·2, 1·0, 0·9 1·1, 1·1, 1·1, 1·3, 0·8, 0·8, 0·6, 0·5, 0·5, 0·5, 0·5, 0·5. The gradual acceleration in the rate of absorption may perhaps be attributed to an enhanced solvent action of the bromohydrin solutions on the ethylene, that is, to a progressive increase of the molecular concentration of this reagent. In other series of experiments the corresponding times were noticeably different, and it seems possible that the acceleration or retardation was due to the presence of small amounts of foreign substances.

(2) In order to test the influence of temperature on the reaction

FIG. 1.



it was conducted at 35°, after a preliminary control experiment had been carried out at the same temperature according to the principle indicated above. A constant volume of 250 c.c. was maintained throughout the experiment, water being added to replace the loss by evaporation. The volume of $N/10$-silver nitrate solution required by 5 c.c. of the liquid after the control experiment had been continued for four hours was 0·08 c.c. Thus, at 35° there appears to be a very slow decomposition of hypobromous acid into hydrogen bromide and oxygen, and a corresponding correction was introduced. It was also found necessary, when working at this temperature, to apply a correction for the loss of bromine by diffusion, which amounted to 1·20 grams in the control experiment.

On passing bromine vapour and ethylene into 250 c.c. of water

under the conditions of the control experiment, the amount of bromine utilised in the preparation of a 0·437*N*-solution of ethylenebromohydrin was 28·2 grams, after correcting for the loss by diffusion. Of this amount, 62 per cent. reacted to form ethylenebromohydrin and hydrogen bromide, as compared with 85·4 per cent. reacting in this way, for the same concentration, in the ice-cooled solution. The time taken was 14·5 hours, the corresponding time at the lower temperature being 10·0 hours. It is therefore apparent that by raising the temperature the reaction takes place more slowly, and that at the same time the molecular ratio of ethylenebromohydrin to ethylene dibromide is materially lessened.

The effects just noticed were accentuated at still higher temperatures, but owing to the considerable loss of bromine by diffusion at temperatures much above 35° quantitative examination was rendered difficult in such cases. From further experiments, to be described below, the second effect is somewhat more pronounced than indicated by the above figures, which take no account of the slow hydrolysis of ethylenebromohydrin occurring in warm aqueous solutions. The slower rate of reaction between ethylene and bromine water in warm solutions is probably to be attributed to the diminishing solubility of ethylene in water as the temperature rises.

(3) In the addition of hypochlorous and hypobromous acids to unsaturated substances it has usually been assumed that the reaction is favoured by conducting the operation not only at a low temperature but also in diffused light, or, preferably, in the dark. It was therefore of interest to investigate the influence of light upon the additive reaction between hypobromous acid and ethylene. In the short series of experiments summarised below, the ice-cooled water (530 c.c.) was exposed to direct sunlight during the passage of the bromine vapour and ethylene, and the progress of the reaction was followed in the manner already described. The result of a control experiment indicated that no appreciable decomposition of hypobromous acid took place under the conditions laid down.

Stage.	Total bromine present (grams).	Total bromine present as $C_2H_4Br{\cdot}OH$ +HBr (grams).	Concentration of ethylene-bromohydrin (*N*).	Percentage of total bromine reacting to form $C_2H_4Br{\cdot}OH+HBr$. In sunlight.	In diffused light.
1	4·12	3·81	0·045	92·5	93·5
2	12·38	10·97	0·130	88·6	91·7
3	20·35	17·80	0·212	87·5	90·0
4	36·59	30·75	0·368	84·0	86·8

From the last two columns of the table it is seen that the values obtained in this series of experiments for the molecular ratio of

ethylenebromohydrin to ethylene dibromide are slightly lower than the values corresponding with the original conditions; the differences, however, are not marked. The time taken for the absorption was 2·75 hours, which is appreciably less than any corresponding period observed for an experiment conducted in diffused light. On the whole, therefore, the rather remarkable conclusion is reached that sunlight exerts an advantageous rather than a detrimental influence upon the additive reaction between hypobromous acid and ethylene.

Physical Properties of Pure Ethylenebromohydrin.

Ethylenebromohydrin is a colourless, mobile liquid, miscible with water in all proportions. Demole's statement (*loc. cit.*) that it is only sparingly soluble in water indicates contamination with ethylene dibromide. The solubility in water decreases considerably in the presence of certain salts, such as, for example, sodium chloride, calcium chloride, and sodium sulphate. The aqueous solutions possess a sweet, burning taste. The vapour of the pure substance or of its aqueous solutions, down to about 5 per cent. strength, produces a painful irritation of the eyes and nostrils shortly after inhalation. Ethylenebromohydrin dissolves readily in most of the common organic solvents, but forms a distinct phase when added to light petroleum. It distils unchanged under diminished pressure at the temperatures noted above; when the pure substance is heated under atmospheric pressure, however, it darkens as the temperature approaches the boiling point, and decomposition occurs with the production of hydrogen bromide. Distillation commences at about 150°, but the temperature fluctuates and the boiling point is indefinite.

The refractive index of several specimens was determined with the Abbé refractometer at 20° for the *D* line; the results were practically identical, the mean value being 1·4915. When the liquid was exposed for a few seconds on the prism this value sank in a typical instance to 1·479; this observation illustrates the pronounced hygroscopicity of ethylene bromohydrin. The observed molecular refractive power at 20° was 34·84, which stands in close agreement with the calculated value, 34·76.

Determinations of specific gravity (reduced to a vacuum) were as follows:

D_4^0 1·7902, D_4^{15} 1·7696, D_4^{20} 1·7629, D_4^{25} 1·7560, D_4^{30} 1·7494.

The mean coefficient of dilatation between 0° and 30°, calculated from the data obtained in the above determinations, is 0·00078.

The Relationship between the Refractive Index and the Concentration of Aqueous Solutions of Ethylenebromohydrin.

It has been shown by Irvine that measurements of refractive index provide a rapid and convenient method for the determination of the approximate strengths of aqueous solutions of ethylenechlorohydrin; the method has also been adopted, with useful results, by Gomberg (*loc. cit.*, p. 1418). For this reason, and also in view of certain interesting thermal changes and related phenomena which occur during the dilution of ethylenebromohydrin with water, it was considered advisable to undertake a refractometric examination of a series of aqueous solutions of this substance. Solutions of different concentrations were made by direct weighing of the constituents, and in each case the refractive index was determined with the Abbé instrument at 20° for the *D* line. Some of the observations are tabulated herewith:

Percentage by weight of ethylene-bromohydrin.	n_{D}^{20}.	Percentage by weight of ethylene-bromohydrin.	n_{D}^{20}.
100·000	1·4915	49·179	1·3915
95·340	1·4801	40·372	1·3790
90·032	1·4671	30·999	1·3667
80·007	1·4454	22·441	1·3561
72·201	1·4299	18·810	1·3517
60·586	1·4095	10·010	1·3422
53·620	1·3980	3·361	1·3358
		0 (water)	1·3330

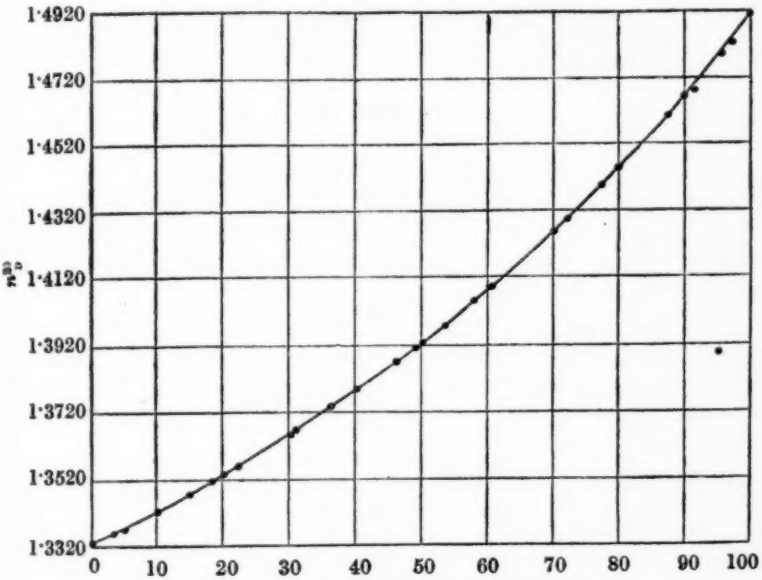
When the whole of the data are represented graphically, the resulting points lie on a regular curve which does not approximate to a straight line (Fig. 2). The character of the curve indicates that the refractive index of aqueous solutions of ethylenebromohydrin is always less than the value calculated from the admixture formula, that is, on mixing ethylenebromohydrin with water there is a contraction in volume. It is also to be observed that the value of the refractive index does not pass through a maximum, as in the case of ethyl alcohol (Doroschevski and Dvorschantschik, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 908). It is evident that the above curve furnishes a ready means of determining, with close accuracy, the concentrations of aqueous solutions of ethylenebromohydrin.

The Distillation of Aqueous Solutions of Ethylenebromohydrin.

From the general characteristics of ethylenebromohydrin it seemed probable that its dilute aqueous solutions, such as are obtained in the method of preparation outlined above, might be

concentrated by fractional distillation. In order to test this point, solutions of known strength were submitted to this operation, the various fractions being examined refractometrically. In the case of a 5 per cent. solution a first fraction, containing 3 per cent. of the total bromohydrin, had a concentration of 12 per cent. The concentrations of succeeding fractions were lower; when 20 per cent. of the total bromohydrin had been collected, the concentration of the next few drops of distillate was 9·5 per cent., and after the collection of 50 per cent. the corresponding value was 7·0 per cent.

FIG. 2.



The boiling point was originally 100·0°/766 mm., and it rose eventually to 100·1°. The boiling point of water at the same pressure is 100·22°.

With a 30 per cent. solution a first fraction, containing 11 per cent. of the total bromohydrin, had a concentration of 34·0 per cent., and when two-thirds of the total bromohydrin had passed over the concentration of the next few drops of distillate was identical with that of the original solution, that is, 30 per cent. Meanwhile, the boiling point had risen from 99·0° to 99·4°; the barometric height was 768·5 mm., corresponding with a boiling point of 100·31° for water.

These observations suggested that ethylenebromohydrin forms a mixture of constant boiling point with water at a concentration in the vicinity of 34 per cent. A similar distillation of a 34 per cent. solution confirmed this conclusion, the actual concentration of the constant-boiling mixture being 35·0 per cent., as is evident from the following table:

Fraction.	Boiling point.	Weight of fraction (grams).	n_D^{20}.	Concentration per cent. of bromohydrin in fraction.	Percentage of total bromohydrin in fraction.
1	99·1	0·90	1·3718	35·1	3·0
2	99·1	2·06	1·3720	35·2	6·9
3	99·1	2·96	1·3717	35·0	9·8
4	99·1	3·22	1·3717	35·0	10·7
5	99·2	3·38	1·3716	34·9	11·2
6	99·2	3·44	1·3714	34·8	11·3
7	99·2	4·24	1·3708	34·3	13·7
8	99·5	4·35	1·3700	33·7	13·9
residue	—	6·11	1·3700	33·7	19·5

The constant boiling point of a 35·0 per cent. aqueous solution of ethylenebromohydrin is therefore 99·1°/762·4 mm., the corresponding boiling point of water being 100·06°. The residue from the above distillation possessed a faint yellow colour, and was distinctly acid; titration with standard silver nitrate solution showed that it contained 0·1491 gram of hydrogen bromide, evidently produced by partial hydrolysis of the bromohydrin during the distillation. The distillates contained a mere trace of the acid, and thus the percentage amount of the total bromohydrin hydrolysed in the course of the operation was 2·2.

Very interesting results were obtained by distilling more concentrated solutions of the bromohydrin, and a typical series of data is accordingly summarised below for the case of a 74·9 per cent. solution. The barometric height was 755 mm., corresponding with a boiling point of 99·82° for water.

Fraction.	Boiling point.	Weight of fraction (grams).	n_D^{20}.	Concentration per cent. of bromohydrin.	Percentage of total bromohydrin in fraction.
1	99·5°	1·08	1·3798	41·0	2·0
2	100·0—101·0°	3·03	1·3838	43·9	6·1
3	101·0—102·8	3·70	1·3880	47·0	8·0
4	102·8—109·1	3·84	1·3982	53·9	9·5
5	109·1—137·0	3·81	1·4332	74·0	12·9
6	137·0—147·4	4·51	1·4840	97·0	20·0
7	147·4—149·0	5·26	1·4912	99·9	24·0
residue	—	3·83	1·4905	99·7	17·5

When concentrated aqueous solutions of ethylenebromohydrin are distilled the water thus passes over in the initial stages of the operation, and eventually almost pure bromohydrin distils. In the

experiment described it was ascertained by titration that 0·9 per cent. of the total bromohydrin present was hydrolysed during the distillation. Of the hydrogen bromide formed it is interesting to note that 5 per cent. remained in the distilling flask, and 5 per cent. was present in fraction 5; the bulk was found in fractions 6 (60 per cent.) and 7 (30 per cent.). As fractions 6 and 7 thus contained 1·7 and 0·7 per cent. of hydrogen bromide respectively, the purity was distinctly lower than indicated by the refractive index. From these investigations it is seen that dilute aqueous solutions of ethylenebromohydrin might be concentrated by fractional distillation, but that in dealing with large quantities of such solutions the loss by hydrolysis would be considerable. This objectionable feature could be partly eliminated by conducting the distillation under diminished pressure.

The Hydrolysis of Ethylenebromohydrin.

The slight decomposition noticed during the distillation of aqueous solutions of ethylenebromohydrin seemed to indicate a greater susceptibility of this substance towards hydrolysing agents than is exhibited by ethylenechlorohydrin, and accordingly further observations were made in order to settle this point.

In the first place, when aqueous solutions of ethylenebromohydrin of concentrations ranging from 95 per cent. to 3 per cent. were prepared and examined at regular intervals no decomposition could be established until several weeks had elapsed. As a typical example, a 50 per cent. solution after remaining for a month at the ordinary temperature had developed a perceptible content of hydrogen bromide, corresponding with the hydrolysis of about 0·3 per cent. of the bromohydrin originally present; in the same period the refractive index had declined by 0·0007. With a 3 per cent. solution the amount hydrolysed in the same time approached 1 per cent. of the bromohydrin, and in general this very slow hydrolysis was most apparent in dilute solutions. At higher temperatures the velocity of hydrolysis in aqueous solution was much accelerated; on boiling a 6·25 per cent. solution for thirty minutes under reflux, 19 per cent. of the bromohydrin was hydrolysed, and in ninety minutes 44 per cent. was hydrolysed.

Silver nitrate produced no immediate reaction with cold aqueous solutions of the bromohydrin, but in dilute solutions an opalescence developed after fifteen or twenty minutes, and quantitative estimations made after longer intervals showed that the hydrolysis had undergone appreciable acceleration.

Seeing that ethylenebromohydrin is prepared in acid solution, it was of interest to ascertain the effect of acid on the rate of hydro-

lysis. A 1·8*N*-solution of hydrochloric acid containing 9·0 per cent. of ethylenebromohydrin was examined twenty-four hours after being prepared, but no perceptible hydrolysis had occurred in the cold. By boiling this solution for thirty minutes, 51 per cent. of the bromohydrin was hydrolysed, the presence of acid having therefore accelerated the reaction.

It was to be anticipated that alkali would exert a much more pronounced acceleration than acid, and, in fact, a 4·5 per cent. solution of ethylenebromohydrin, containing about two equivalent proportions of potassium hydroxide, was hydrolysed to the extent of 47 per cent. when allowed to remain at the ordinary temperature for thirty minutes. By boiling a similar solution for thirty minutes, 97 per cent. of the bromohydrin was hydrolysed, and ninety minutes' boiling brought about complete hydrolysis.

Lastly, an analysis of a pure specimen of ethylenebromohydrin by alkaline hydrolysis may be quoted: 0·2935 gram, after boiling for ninety minutes with an excess of sodium hydroxide solution, required 23·5 c.c. of $N/10$-$AgNO_3$. Br = 64·0. Calc., Br = 64·0 per cent.

Summary.

1. Pure ethylenebromohydrin has been prepared in quantity by the action of cold dilute bromine water on ethylene, this method having been found preferable to any other which has been described for the purpose.

2. In the above reaction the molecular ratio of ethylenebromohydrin to ethylene dibromide decreases continuously with increasing concentration of ethylenebromohydrin and hydrogen bromide in the solution, and also with rise of temperature, but it is not influenced markedly by sunlight. The reaction is hastened by cooling or by exposure to sunlight.

3. The main physical characteristics of ethylenebromohydrin, and also the relationship between the concentration and refractive index of its aqueous solutions, have been established.

4. Ethylenebromohydrin and water form a mixture of constant boiling point (99·1°/762·4 mm.) at a concentration of 35·0 per cent.

5. Ethylenebromohydrin is hydrolysed more readily than ethylenechlorohydrin. In cold aqueous solutions the hydrolysis is perceptible, although extremely slow; it is greatly accelerated by heat, also by the presence of acid, and, notably, of alkali.

Cognate investigations are in progress.

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CXXXIII.—*The Propagation of Flame in Mixtures of Methane and Air. Part II. Vertical Propagation. Part III. Propagation in Currents of the Mixtures.*

By Walter Mason and Richard Vernon Wheeler.

Part II.—Vertical Propagation.

The object of the experiments herein described on the vertical propagation of flame in mixtures of methane and air was to obtain information as to the magnitude of the effect of convection currents on the speed of the flame.

Except, perhaps, during the "uniform movement,"* the transference of heat by convection currents clearly plays an important part in the transmission of flame, and is accountable for many of its phenomena. For example, the well-known fact that the limits of inflammability of gaseous mixtures vary with the position of the point of ignition according as the flame has to pass upwards or downwards through the mixture, more combustible gas being required to form a lower-limit mixture under the latter conditions, is explicable on the assumption that during the downward propagation of flame convection currents do not materially affect the transference of heat to unburnt layers of the mixture. A like explanation can be given for the fact that when mixtures of methane and air containing less than 7·5 and more than 12·5 per cent. of methane are ignited at the centre of a closed spherical vessel, flame reaches the bottom of the vessel later than it reaches the top by an interval of time which varies with the methane-content of the mixture (T., 1918, **113**, 845).

In general, it would seem probable that flame should travel vertically in a given mixture more rapidly when it is ignited from below than when it is ignited from above, if only by virtue of the current produced by the heated gases. Under the special conditions of ignition at the centre of a closed vessel, however, any difference there may be between the speeds of upward and downward propagation of flame is inappreciable with mixtures in which

* The "uniform movement" is the term generally applied to the initial slow propagation of flame at a uniform speed that occurs when an inflammable mixture is ignited at the open end of a horizontal tube closed at the other end. Under such conditions the propagation of flame is assumed by Le Chatelier to be "normal" and to be effected mainly by the conduction of heat from the burning to the unburnt gases.

the speed of flame is comparatively rapid (mixtures containing between 7·5 and 12·5 per cent. of methane). As bearing on this point, certain observations by Schloesing and de Mondésir on the combustion of mixtures of carbon monoxide and air should be noted. Having remarked that one rarely observes the "normal" propagation of flame because of the development of movements in the gaseous mixtures due to the combustion itself, they suggest that one of the principal causes of movement or agitation of the burning mixture is the difference in density between the heated and the cold gases: "Un mélange gazeux allumé par la partie inférieure, brûle toujours plus vite que lorsqu'il est allumé par la partie supérieure. Les gaz chauds s'élèvent en effet à travers les gaz froids avec une vitesse qui vient s'ajouter à la vitesse normale de propagation. Mais l'accélération ainsi produite est toujours très faible; elle n'est sensible qu'avec les mélanges gazeux très lents et renfermés dans des tubes de grand diamètre" (*Ann. des Mines*, 1883, [viii], **4**, 298).

As regards the "uniform movement" (that is to say, "normal" propagation of flame), we drew the conclusion (T., 1917, **111**, 1053) that if Le Chatelier's definition of it as "le mode de propagation par conductibilité" be accepted, it is a strictly limited phenomenon obtainable only in tubes within a certain range of diameter, large enough to prevent appreciable cooling by the walls, but narrow enough to suppress the influence of convection currents, so that the diameter of the tube in which the flames travel should be specified when speeds purporting to be those of the "uniform movement" or "normal" propagation of flame are recorded. Alternatively, the initial slow movement of flame at a uniform speed should be regarded simply as a particular phase in the propagation of flame that occurs when ignition is effected (in a quiescent mixture) at the open end of a straight, horizontal tube (of any diameter) closed at the other end, and not as resulting from a particular mode of heat transference.* As a result of the present investigation, it is shown that the latter is the preferable, if not the only correct, way of regarding the uniform movement; for the idea that this "normal" propagation of flame is solely by conduction of heat from layer to layer of the mixture is untenable. Further, it is shown that there is a uniform régime in the propagation of flame from the open to the closed end of a straight tube

* The influence of convection currents is noticeable with the fastest flames in mixtures of methane and air in tubes 10 cm. in diameter, the visible effect being a turbulence of the flame-front; whilst in tubes of smaller diameter (5 to 9 cm.), although there is no turbulent appearance, the shape of the flame-front shows that there is a definite movement of the hotter gases towards the upper part of the tube (T., 1914, **105**, 2609).

when the tube is vertical and the direction of travel of the flame is either upwards or downwards.

I. *Ignition at the Open End of a Vertical Tube Closed at the other End.*—Under these conditions, the first phase in the propagation of flame in a horizontal tube is the uniform movement. If this uniform movement of flame in a horizontal tube represents essentially the transference of heat by conduction from layer to layer of the mixture, similar conditions of ignition with a vertical tube should produce a similar uniform movement when the open end of the tube is above, so that the flame travels downwards; for convection currents cannot then be held to play a greater part in the transference of heat to the unburnt mixture than when the flame is travelling horizontally. Moreover, the initial speeds of the flames in like mixtures during their downward propagation in a vertical tube and during the uniform movement in a horizontal tube should be approximately the same, at all events in narrow tubes in which the action of convection currents during horizontal propagation may be assumed to be at a minimum.

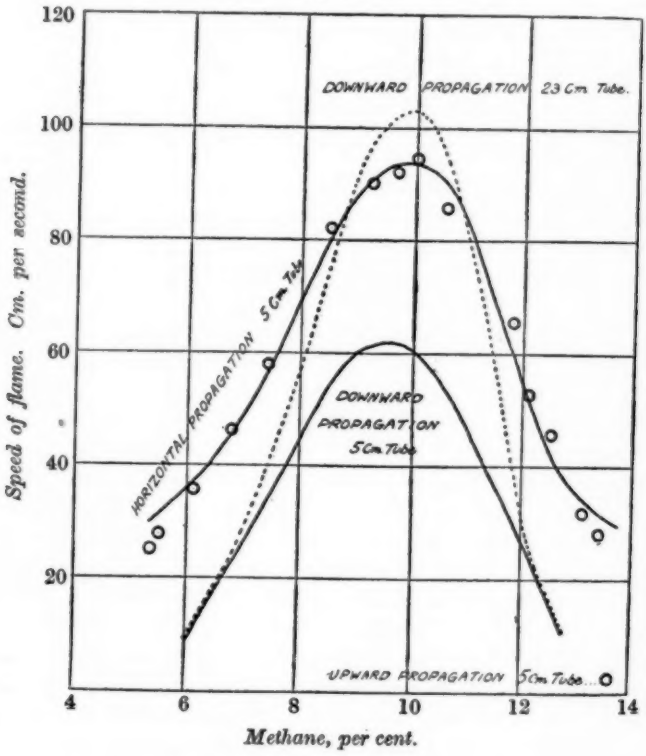
During upward propagation, on the contrary, the initial speeds of the flames should be faster than during the "normal" uniform movement in a horizontal tube, and it would seem unlikely that any phase in the propagation of flame corresponding with the uniform movement would be of long duration.

A glass tube 5 cm. in diameter and 5 m. long was employed for the first series of experiments, with "screen-wires" for recording the speeds of flames stretched across at intervals of 50 cm. Ignition was at a 5 mm. spark-gap 4 cm. from the open end of the tube, and the first screen-wire was stretched at a distance of 20 cm. from the point of ignition. The mouth of the tube was provided with a flange ground to receive an end-piece, which was held in position by metal clips whilst the tube was being filled with the mixture. Before igniting the mixture, this end-piece was slid gently to one side in such a manner as to avoid causing disturbance of the gases within the tube. The method of recording the times of fusion of the screen-wires, and the general mode of procedure for similar experiments, are described in T., 1914, **105**, 2609.

As anticipated, the speeds at which the flames travelled downwards were, with all the mixtures employed, uniform over a considerable distance from the point of ignition. A vibratory movement began, in general, somewhat earlier than during horizontal propagation in a tube of the same diameter, but with no mixture was the distance travelled by the flame at a uniform speed less than 100 cm., and with those containing the lower percentages of methane it sometimes exceeded 200 cm.

As regards the magnitudes of the speeds, however, our expectation (based on the assumption that the propagation of flame during the uniform movement in a horizontal tube of small diameter is mainly by conduction of heat) was falsified. In Fig. 1 the results obtained for downward propagation of flame are recorded as a speed-percentage curve for comparison with the curve for the uniform movement in a horizontal tube of the same diameter.

FIG. 1.



Both curves are of the same type, but the speeds of the flames during the initial stage of downward propagation are, over the whole range of inflammable mixtures, but two-thirds the speeds during the uniform movement.

Presumably, then, the transference of heat by convection plays a considerable part in aiding the propagation of flame during the (horizontal) uniform movement even in fairly narrow tubes. This being so, it seemed probable that, contrary to our first assumption, the speed of propagation of flame upwards would be not much, if

any, faster than during horizontal propagation, unless further benefit from convection currents is obtained during the former conditions.

Measurements of the speeds during the upward propagation of flame were not easily made by the method of screen-wires except at or near the limits of inflammability. Over most of the range of inflammable mixtures the flames sometimes began to vibrate violently within 50 or 60 cm. of the open end of the tube. From the moment of ignition, however, the flames, even those that travelled fastest, seemed to move at uniform, or but slightly accelerating, speeds. Attempts were therefore made to measure these speeds, the first screen-wire being placed 10 cm. from the point of ignition and the succeeding wires at distances of 25 cm. from each other. The results were rather irregular. The speed of the flame between the first and second screen-wires was sometimes enhanced by the impetus given by the source of ignition, a distance of travel of 10 cm. being barely sufficient to allow this impetus to die away, and a vibratory movement often began at or before the third screen-wire. However, the measurements were consistent enough to show that over the comparatively short period during which the speed of the flame travelling upwards could be regarded as constant, that speed, for any mixture of methane and air, was not greater than during the uniform movement in a horizontal tube; it was sometimes less.

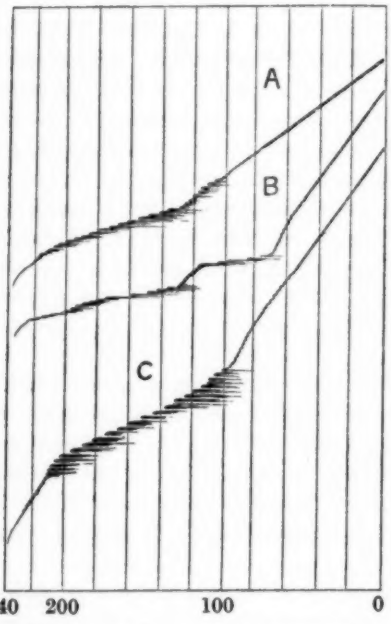
The results are inserted in Fig. 1 as approximate points marked by circles. With the mixtures near the limits of inflammability, such as those containing 5·45, 5·55, and 13·4 per cent. of methane, the flames travelled over a distance of 200—300 cm. at uniform speeds which could be determined accurately, and were distinctly slower than those of the uniform movement in corresponding mixtures in a horizontal tube.

To confirm these results, two series of determinations of speeds of flames in a number of mixtures of methane and air were made by photographing on a rapidly revolving film the illumination of a quartz window in a brass tube 5 cm. in diameter, along which the flames travelled, (1) horizontally, and (2) vertically upwards (see this vol., p. 37). As thus measured, the speeds over the whole range of mixtures were from 3 to 5 cm. per second less when the flames travelled upwards than when they travelled horizontally. Probably this slight difference in the speeds arises from the difference there is in the shape of the flame-front; when travelling horizontally the flame-front has an elliptical cross-section (see T., 1914, **105**, 2609, Fig. 2), whereas when travelling upwards it is circular, so that in a tube of given diameter the circumference of

the flame-front relative to its area is greater with an upward- than with a horizontally-moving flame, and the cooling effect of the walls of the tube is correspondingly greater. Since with flames travelling horizontally the length of the major axis of the elliptical flame-front is at its maximum with mixtures near the limits of inflammability, the maximum difference in speed between upward- and horizontally-moving flames in a tube of given diameter should be found with such mixtures. This is so.

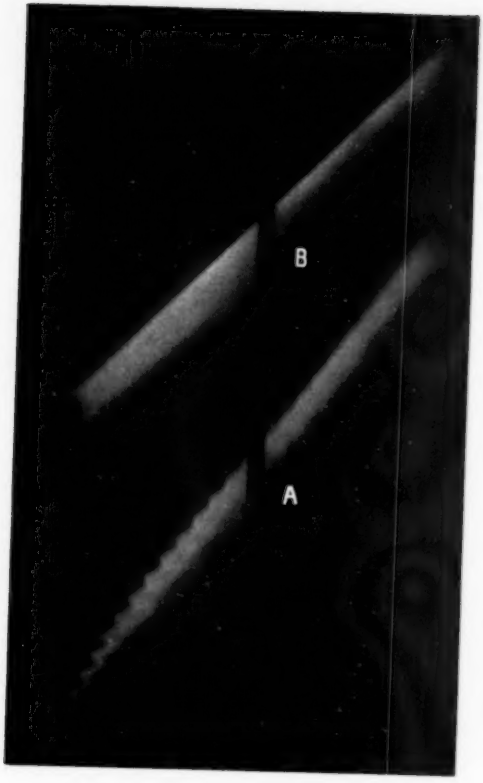
Diagrammatic representations of the complete progress of the flames travelling in a 10 per cent. mixture of methane and air from end to end (240 cm.) of the brass tube with a quartz window are given in Fig. 2. These diagrams have been reduced in size from tracings taken from the actual photographs, which measured 60 × 40 cm., and were obtained in the manner described in Part I of this research. For the purpose of comparison, the flames should be regarded as travelling from right to left of the diagram and the photographic film as moving vertically upwards; actually, the flame was moving vertically upwards for *A*, vertically downwards for *B*, and horizontally for *C*. The last-named is a tracing of the photograph reproduced as Fig. 1, Plate I, on p. 66 of this volume. The rate of revolution of the film was not the same for each set of photographs, so that direct comparison of the speeds of the flames cannot be made from the diagrams, which, however, show clearly that the general behaviour of a flame travelling from the open to the closed end of a tube is not dependent on the position of the tube.

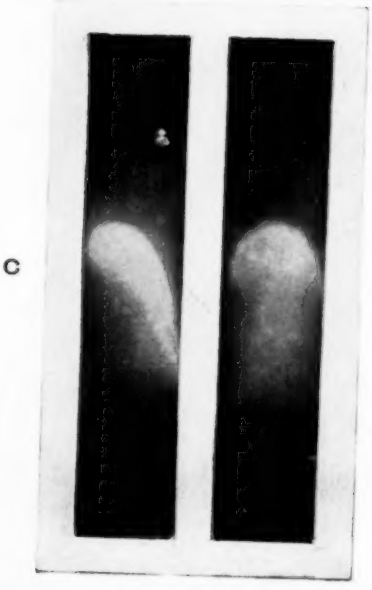
FIG. 2.



Distance along the tube, measured from the point of ignition. Cm.

We have already commented on the irregularity of some of the results obtained when attempting to measure the initial speeds of the flames by the screen-wire method during upward propagation.





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The reason for the irregularity under such conditions of experiment became apparent when the movement of the flames was photographed. For it was found that with mixtures containing between 9·0 and 11·0 per cent. of methane the flames were very sensitive to the effect of resonance of the tube, and could acquire either of two speeds (but not speeds intermediate between the two). If resonance was set up in the usual way, by the movement of the flame along the tube, the speed of the flame was normal, but if by some action on the part of the experimenter the tube was caused to resonate at, or very shortly after, the moment of ignition, the mean speed of the flame was 20 cm. per second slower than normal. It has already been observed, and is, in fact, apparent from the photographs and diagrams, that the incidence of resonance retards the general forward movement of the flame until such time as a certain degree of turbulence is imparted to the mixture.

This retarding effect is well illustrated by the photographs reproduced in the Plate, which show the progress of the flame in a 9·7 per cent. mixture of methane and air in the brass tube over the distance 25—55 cm. from the point of ignition, (*A*) when the tube was resonating, and (*B*) when it was not. The photographs were taken within a few minutes of each other on the same film, which was revolving at the same speed in each instance.

Further information as to the difference in character between the two flames was obtained from photographs showing the shape of the flame-front (see Plate). A quartz tube, 5 cm. in diameter, was fixed vertically and covered with black paper except for a slit, 2·5 mm. broad, at right angles to the axis of the tube and 25 cm. from the open end (the lower end), at which ignition was effected. Flames travelling up the tube, in a mixture containing 8·3 per cent. of methane, were photographed, as they passed the slit, on a film which also travelled upwards. As each portion of the flame-front appeared at the slit it was thus photographed on a fresh portion of the film and its shape was recorded. The arrangement of the quartz lens used to focus the slit on the photographic film was such that an image one-quarter the size of the object was obtained; the speed of the film was therefore regulated to be as nearly as possible one-quarter that of the flames, so as to preserve their relative proportions. It will be seen that in *C*, when the tube was resonating, the undulations of the flame-front are well defined and it is unsymmetrical; in *D*, when the tube was not resonating, the flame-front is quite symmetrical.

The important point to have established is that a phase in the propagation of flame during which the speed is uniform is obtained when the flame travels from the open to the closed end of a tube,

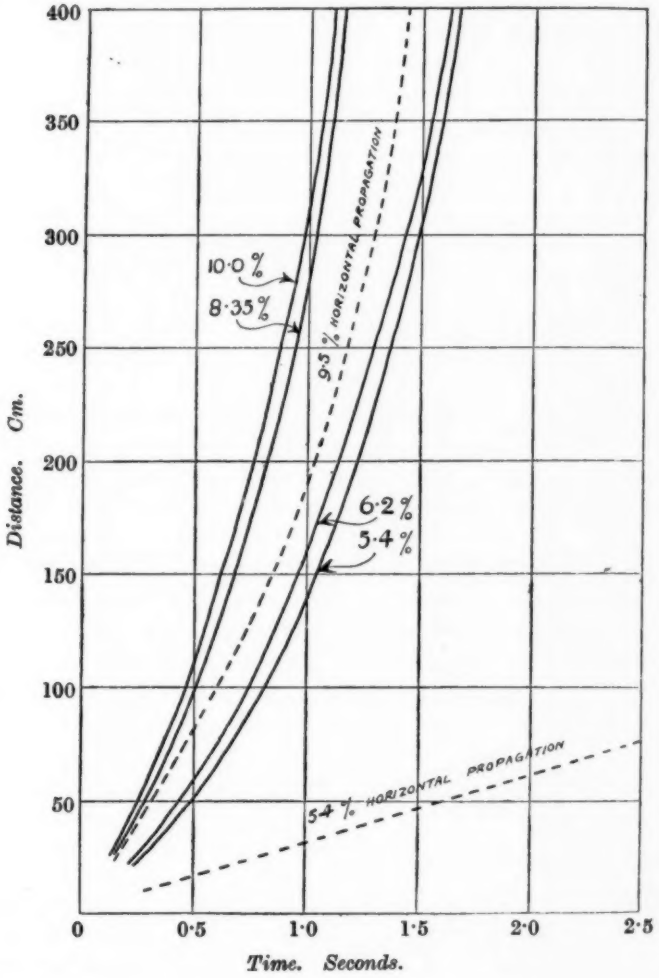
whether the direction of travel is horizontal, vertically upwards, or vertically downwards, and that this uniform speed for any given mixture is slowest during downward propagation. This means that it is not permissible to regard the "uniform movement" (that is to say, the phase of uniform speed of flame during horizontal propagation) as representing "la vitesse normale de propagation de la flamme par conductibilité." If propagation of flame solely by conduction of heat obtains at all, our experiments show that it is most likely to occur when the flame travels downwards, the effect of convection currents being assumed then to be negligible.

When travelling downwards in a glass tube 5 cm. in diameter, the flame-front during the period of uniform speed of propagation of flame is, with all mixtures of methane and air, a steady, or but gently undulating, disk. There is no suspicion of turbulence such as makes its appearance with the more rapid flames when they travel horizontally in such a tube. It seemed possible, therefore, that, if convection currents do not materially assist the flame in its propagation downwards, a considerable increase in the diameter of the tube down which the flames travel could be made without their speeds being augmented. On trial, however, using a metal tube 23 cm. in diameter and 7 m. long, it was found that with mixtures containing more than 7 and less than 12 per cent. of methane the speeds of the flames were considerably greater than in a glass tube 5 cm. in diameter, as the curve in dotted line in Fig. 1 shows. With the mixtures containing between 9 and 11 per cent. of methane, the ratio between the speed of the flame and the diameter of the tube was nearly the same as when the flames travel horizontally (see Fig. 3, T., 1917, **111**, 1052). However it may be during the downward propagation of flame in mixtures containing less than 7 or more than 12 per cent. of methane, it is obvious, therefore, that something other than conduction of heat is responsible for the development of the more rapidly moving flames in the tube of larger diameter. The enhanced speeds of the flames as they travel downwards in the larger tube are no doubt due to turbulence of the flame-front engendered by convection or eddy currents.

We can, then, fully endorse Schloesing and de Mondésir's statement that the normal propagation of flame is rarely observed when the word "normal" is taken to imply "by conduction of heat." It is highly abnormal that such a mode of heat transference should alone be operative during the propagation of flame. In so far, therefore, as the term "uniform movement" of flame has been held to be the normal propagation of flame by conduction of heat, it ought to be discarded. The term is, however, a useful

one, and fittingly describes a phase in the propagation of flame (obtainable under a variety of conditions, which should be specified) the identification and measurement of which is of considerable

FIG. 3.

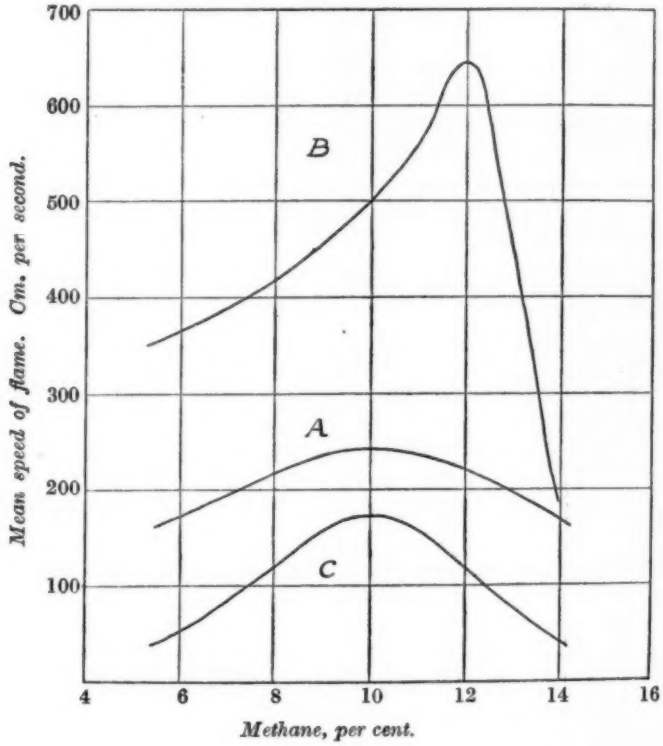


value. As a name, without implying a mode of heat transference during the phenomena it describes, there is no reason why it should not be retained, and it may be convenient to do so.

II. *Ignition at One End of a Vertical Tube Open at both Ends.*—Under these conditions, the tube in which the flame travels

becomes a "chimney," and there is added to the speed of a flame travelling up the tube the speed of the draught produced by the chimney. In addition, the mechanical effect of this draught in promoting turbulence of the mixture probably augments the speed of the flame. Flame does not pass downwards if the mixture is ignited at the top of the tube, but continues to burn at the mouth until the whole of the mixture has been drawn up.

FIG. 4.



In Fig. 3 are shown time–distance curves for the propagation of flame upwards in several mixtures of methane and air in a vertical glass tube 5 cm. in diameter and 5 m. long, open at both ends. These curves should be compared with those obtained when the tube was horizontal (Fig. 1, this vol., p. 42). The character of both sets of curves is similar, and indicates a gradual and regular acceleration of speed as the flame travels from end to end of the tube. This acceleration occurs with the lower-limit mixture (5·4

per cent. of methane) when the flame travels upwards, a result which displays clearly the chimney effect of the tube, for the speed of the flame in the lower-limit mixture is quite uniform when it travels horizontally.

The speeds of the flames at all stages of their propagation are considerably faster during upward than during horizontal propagation, for the reasons already given. Fig. 4 records the mean speeds over measured distances for the whole range of inflammable mixtures: (*A*) for the distance 50—100 cm. measured from the first screen-wire, which was 10 cm. from the point of ignition, and (*B*) for the distance 200—300 cm. A curve (*C*) showing the mean speed over the distance 50—100 cm. during horizontal propagation in the same tube is given for comparison.

Curve *B* presents a characteristic novel to these investigations on the propagation of flame in mixtures of methane and air, inasmuch as the maximum speed of flame is found, not, as is usual, with mixtures containing between 9·5 and 10·5 per cent. of methane, but with those containing about 12 per cent. This result, which is, of course, due to the chimney effect of the tube, is probably quite adventitious; with the particular diameter and length of tube employed, the chimney effect assumed a maximum with mixtures containing about 12 per cent. of methane, perhaps by reason of the composition of the products of combustion of those mixtures.

III. *Ignition at the Closed End of a Vertical Tube Open at the other End.*—When the mixture is ignited at the closed end of a tube open at the other end, the position of the tube does not affect the results. The results obtained when the tube is horizontal have been described in Part I.

Part III.—The Propagation of Flame in Currents of Mixtures of Methane and Air.

The object of these experiments was: (i) to determine whether the fact that the gases were moving as a current would simply add to the speed of the flame the speed of that current, or whether an effect of turbulence would be introduced, and (ii) to see if a smaller quantity of methane than that which forms the lower-limit mixture (5·4 per cent. for horizontal or upward propagation of flame) in a still atmosphere would be capable of conveying flame from one place to another if the mixture itself were moving.

(i) The experiments with a vertical tube open at both ends, described in Part II of this research, had shown that the speed of

the current induced in such a tube, acting as a chimney, was added to the speed of a flame travelling upwards in it, and it was assumed that turbulence caused by the current further increased the speed of the flame, though no proof of this could be given, since the velocity of the current was indeterminate.

A tube 2·5 cm. in diameter and 220 cm. long was fixed horizontally and connected by rubber tubing to a large metal gasholder, a short brass tube with a disk of metal gauze at either end being interposed to prevent flame travelling back into the holder. Streams of a mixture of methane and air could be caused to pass at different speeds along the tube, both ends of which were open, by varying the counter-weights on the bell of the holder and opening the wide-bore metal tap thereon to its full extent. The mixtures were ignited electrically at a point 26 cm. from the connexion to the brass tube, and the speeds of the flames were measured by means of screen-wires, the first screen-wire being 50 cm. from the point of ignition.

A mixture containing 6·35 per cent. of methane was used, as being one in which the speed of flame in a still atmosphere under the conditions of the experiments would not be excessive in comparison with that of the currents that could be produced. The results, giving the mean speeds of the flames over 100 cm., were as follow:

Speed of current. Cm. per second.	Speed of flame. Cm. per second.	Difference. Cm. per second.
Nil	287	287
23	582	559
43	952	909
75	1527	1452

It is thus apparent that the major effect of the current is that of turbulence. The fact that such a comparatively gentle movement of the mixture as is represented by a speed of 23 cm. per second should nearly double the speed of the flame is very striking and emphasises the important part that convection currents must play in the transmission of flame.

(ii) When a homogeneous mixture of methane and air containing between 4 and 5 per cent. of methane is caused to travel slowly over a small flame, such as that of a candle, flares of flame of burning methane are produced which follow the direction of the current, and may extend for a considerable distance—a distance greater than the length of the "cap" produced by a similar mixture around such a flame in a still atmosphere. These flares of burning methane may even become detached from the source of heat around which they form and float away for a short distance in the stream of mixture (T., 1914, **105**, 2594).

We had also obtained evidence that if a sufficient degree of turbulence is produced in a closed vessel, by means of a rapidly revolving fan, in a mixture of methane and air containing not less than 5·0 per cent. of methane, flame will travel throughout the mixture, following the current induced by the fan (T., 1914, **105**, 2595). Since the effect of causing a mixture of methane and air to travel along a tube at a fairly slow speed is to impart turbulence to the mixture, and since the degree of turbulence thus imparted is sufficient greatly to increase the speed of propagation of flame in (that is to say, the rate of combustion of) the mixture, it seemed probable that the lower limit of inflammability, which is partly dependent on the rate of combustion of the gas, might be less with a slow stream of methane and air than with a quiescent mixture, just as the lower limit is less for upward propagation of flame (5·4 per cent.), when the combustion is aided by convection currents, than for downward (6·0 per cent.).

A horizontal glass tube 5 cm. in diameter and 320 cm. long was used for the experiments, which were conducted in a similar manner to those already described. The point of ignition was 17 cm. from the brass tube connecting the glass tube to the gas-holder, and the first screen-wire was 35 cm. from the point of ignition. The experiments were as follow:

(*a*) CH_4, 5·15 *per cent.*—Speed of current, 65 cm. per second. A flame, about 2·5 cm. long, travelled the whole length of the tube occupying the upper half of it. The speed of the flame increased gradually over the last 200 cm. from 75 to 85 cm. per second.

(*b*) CH_4, 5·10 *per cent.*—Speed of current, 65 cm. per second. Observations as in previous experiment, the speed of the flame being about 70 cm. per second throughout.

(*c*) CH_4, 5·05 *per cent.*—Speed of current, 65 cm. per second. A more powerful secondary discharge had to be used to ignite this mixture. The flame produced was only 1·2 cm. long, but it travelled the whole length of the tube at a speed of 65 cm. per second—that is to say, at the speed of the current of mixture.

(*d*) CH_4, 5·02 *per cent.*—The intense "flaming" discharge obtained when a Wehnelt electrolytic interrupter is used in the primary circuit of an induction coil had to be used to ignite this mixture. When ignited, a small flame travelled throughout the length of the tube at the speed of the current of mixture, namely, 65, 50, and 35 cm. per second in successive trials. With a faster speed of current (about 80 cm. per second) or a slower speed (about 30 cm. per second), the flame travelled from 200 to 250 cm. and then died out.

(*e*) CH_4, 5·00 *per cent.*—With no speed of current would flame travel more than about 50 cm. from the point of ignition. This was so whether the Wehnelt discharge used to ignite the mixture was maintained or passed momentarily.

Experiments (*d*) and (*e*) were repeated many times, with the same results: a mixture containing 5·02 or 5·03 per cent. of methane does not enable flame to travel in it when it is at rest, but when it is moving as a current along a tube, flame travels in it at the speed of the current. A mixture containing 5·00 per cent. of methane could not be caused to propagate flame under the conditions of the experiments. Mixtures containing 4·95, 4·90, or 4·85 per cent. of methane gave flares of flame extending a few cm. only along the tube.

The scale on which these experiments were conducted is perhaps scarcely sufficient to warrant the conclusion that flame would be carried indefinitely in a homogeneous mixture containing 5·02 per cent. of methane, along the roadway of a mine, for example, so long as a current of from 35 to 65 cm. per second was maintained. The general character of the experiments, however, pointed to a sharp distinction between a mixture (5·00 per cent. methane) obviously incapable of maintaining a flame apart from the source of heat which originated it, and one (5·02 per cent. methane) in which flame was maintained after the igniting source had been withdrawn. The flame would travel along the roof of the roadway.

The concluding parts of this research will deal generally with the effects of turbulence on the propagation of flame in mixtures of methane and air, as produced by the passage of the mixtures as currents along a tube or gallery, and as induced locally by the presence of restrictions in the gallery.

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CXXXIV.—*The Oxidising Properties of Sulphur Dioxide. Part II. Iron Phosphates.*

By William Wardlaw, Sidney Raymond Carter, and Francis Herbert Clews.

The object of the experiments described in the present communication was to determine whether the oxidising action of sulphur dioxide exhibited in concentrated hydrochloric acid solution (Wardlaw and Clews, this vol., p. 1093) was restricted to this acid or was operative in other acid solutions. Phosphoric acid was selected on account of its non-volatility, and its consequent suitability for quantitative measurements.

Experimental.

Experiment with Ferrous Phosphate Solution.

Solutions of ferrous phosphate were prepared by dissolving iron in phosphoric acid (Erlenmeyer, *Annalen*, 1878, **194**, 182) and treating with sulphur dioxide. Essentially, therefore, the method of procedure was practically identical with that previously employed for the investigation of ferrous chloride reactions (*loc. cit.*). As illustrative of the method used, the following details of the first experiment may be given.

One gram of pure iron was dissolved in 50 c.c. of phosphoric acid (D 1·75, 89 per cent. H_3PO_4) contained in a closed flask, a stream of carbon dioxide being continually passed through the apparatus. A colourless solution of ferrous phosphate was thus obtained. The evolution of hydrogen having ceased, sulphur dioxide was passed through the solution at 115°. After about ten minutes, a faint milkiness was seen in the neck of the flask, and in the course of time, particles of sulphur appeared. The solution remained colourless throughout. After the sulphur dioxide had passed for four hours, the gas was removed from the solution by the passage of carbon dioxide. The ferrous and total iron were determined by titration with potassium dichromate solution. The first experiment showed that 8·1 per cent. of ferric phosphate had been formed under the conditions mentioned. In view of the extreme susceptibility of ferrous phosphate to atmospheric oxidation (Erlenmeyer, *loc. cit.*), the oxidation by sulphur dioxide was not unexpected.

Experiments with Ferric Phosphate Solutions.

To determine whether sulphur dioxide had any reducing action on ferric phosphate, 3 grams of ferric phosphate were dissolved in 50 c.c. of glacial phosphoric acid, and sulphur dioxide was passed through the solution, maintained at 115°, for three hours. On analysing the solution, no ferrous iron could be detected. Further experiments on similar lines gave no evidence of reduction of the ferric phosphate. This result seems to agree with the well-known stability of ferric phosphate in the reducing blowpipe flame. A borax bead containing ferric iron is readily reduced, whereas a ferric microcosmic bead is reduced with difficulty.

Experiments with Ferrous-ferric Phosphate Solutions.

The object of these experiments was to determine whether the prolonged action of sulphur dioxide on ferrous phosphate would result in complete oxidation to the ferric state. The mixtures were made by dissolving iron in phosphoric acid, excluding air during the process, and adding a solution of ferric phosphate in concentrated phosphoric acid.

Concentration of iron: approximately 1 gram per 50 c.c. of solution.

Duration of experiments: four hours.

TABLE I.

Temperature, 115°.

Ferric iron. Per cent. Initial.	Ferric iron. Per cent. Final.	Sulphur deposit.
0·0	8·1	Heavy.
12·5	15·7	Moderate.
21·9	24·7	Moderate.
25·0	28·0	Moderate.
39·7	—	Very light.
55·7	56·9	Just noticeable.
100·0	100·0	None.

TABLE II.

Temperature, 150°.

Ferric iron. Per cent. Initial.	Ferric iron. Per cent. Final.	Sulphur deposit.
43·2	45·7	Moderate.
57·1	60·5	Moderate.
63·4	65·2	Light.
72·0	74·2	Light.
79·1	79·9	Just noticeable.
100·0	100·0	None.

The presence of the great excess of phosphoric acid tended to make the titration somewhat difficult, but the character of the sulphur deposit served as a good indication of the progress of oxidation, especially in those cases where it occurred only to a slight extent.

Comparison of the results obtained at the two temperatures suggests that ferrous phosphate would be completely oxidised to

the ferric state, but that at the temperatures used in these experiments the velocity of reaction is becoming slow, with increasing proportion of ferric salt. Hence during the four hours very little oxidation is detected with the higher proportions of ferric iron.

Limit of Oxidation of Ferrous Phosphate.

Experiments to determine the limit of oxidation were carried out in a special apparatus primarily designed for obtaining the velocity of reaction. The reaction vessel consisted of a wide-necked flask of about 600 c.c. capacity fitted with a rubber stopper, through which passed the bearing for a stirrer, a syphon sampling-tube made of capillary tube of fairly wide bore, an inlet tube for the sulphur dioxide, and a water-cooled exit tube. The syphon sampling-tube was connected with a water-cooled 10 c.c. burette, which in turn was connected with a suction pump. The stirrer was fitted with a mercury seal and closed at the end, so that sulphur dioxide could be maintained at a slight pressure in the flask without leakage. A simple device was used to control the pressure of sulphur dioxide in the flask. The gas issuing from a sulphur dioxide syphon was divided by a T-piece, one arm being connected with the reaction flask and the other connected with a gauge-tube containing concentrated sulphuric acid. By allowing the sulphur dioxide to bubble very slowly through the sulphuric acid, the pressure in the reaction flask was maintained at a value greater than atmospheric, the excess pressure being proportional to the height of the sulphuric acid column.

Method of Procedure.—To 250 c.c. of phosphoric acid contained in the flask was added a definite weight of pure iron. A current of carbon dioxide was then passed through the apparatus, and, on warming, the iron dissolved. When solution was complete, the temperature of the thermostat was adjusted to 150°, and the stream of carbon dioxide replaced by one of sulphur dioxide. By closing the exit tube, the pressure of sulphur dioxide was adjusted. Samples of solution were periodically drawn off into the burette, allowed to cool to the ordinary temperature, the volume adjusted, and run into a flask filled with carbon dioxide. The solution was then diluted with 30 per cent. phosphoric acid, and the sulphur dioxide driven off. The volume was made up to 100 c.c. and titrated with $N/20$-potassium permanganate. The titre was assumed to be proportional to the concentration of ferrous iron in the reaction flask at the moment of sampling.

From experiments conducted in this way, a constant ferric content was found to be established at the end of from two to three days, and the following were the results obtained:

(*a*) At a concentration of 7·35 grams of iron per 250 c.c. of phosphoric acid, the mixture contained 36 per cent. of ferric iron.

(*b*) At a concentration of 3·65 grams per 250 c.c., the mixture contained 45 per cent. of ferric iron.

These results differ distinctly from those obtained from the synthetic mixtures of ferrous and ferric phosphates. This difference might conceivably be due to the sulphur formed in the solutions containing initially only ferrous phosphate, which is absent in the case of the synthetic mixtures. Experiments with synthetic mixtures of ferrous and ferric phosphates to which had been added finely divided or colloidal sulphur showed that this had no observable effect on the degree of oxidation by sulphur dioxide. In addition, sulphur was found to have no appreciable reducing power on ferric phosphate in concentrated phosphoric acid solution.

Maquenne (*Bull. Soc. chim.*, 1890, [iii], **3**, 401) has shown that aqueous solutions of phosphorous acid are oxidised by sulphur dioxide completely to phosphoric acid (compare also Wöhler, *Annalen*, 1841, **39**, 252, and Cavazzi, *Gazzetta*, 1886, **16**, 169). The possibility of the reaction

$$2H_3PO_3 + SO_2 = 2H_3PO_4 + S$$

being reversible was not overlooked, but experiments did not confirm this conjecture.

Velocity and Order of Reaction.—Experiments made with the apparatus described above with a view to determine the rate and order of reaction gave no very definite results, probably owing to the disturbing action of sulphur.

Limiting Concentration of Phosphoric Acid.—This has been determined between narrow limits for ferrous phosphate at 100°. The procedure followed was similar to that used in the case of hydrochloric acid solutions (Wardlaw and Clews, this vol., p. 1097). One gram of iron was dissolved in 50 c.c. of phosphoric acid of different concentrations, the values for which were obtained by measuring the specific gravity of the phosphoric acid and calculating the concentrations from the tables (Hager, "Kommentar zür Pharmacopöa Germanica"; Gmelin-Kraut's "Handbuch," Vol. I, Pt. 3). The results are shown in table III.

A gravimetric estimation was made on the solution in expt. 6 according to Finkener's method (*Ber.*, 1878, **11**, 1640), and it was shown to contain 400·7 grams of phosphoric acid per litre, whilst 32·83 per cent. phosphoric acid (expt. 6) contains 397·2 grams per litre. Assuming the iron to be in combination as $Fe(H_2PO_4)_2$ (Erlenmeyer, *loc. cit.*), the free acid in 1 litre of the ferrous phosphate solution was $400·7 - 68·6 = 332·1$ grams.

TABLE III.

Concentration of iron: 1 gram per 50 c.c.
Temperature: 100°.
Duration of experiments: four hours.

Experiment:	1.	2.	3.	4.
Concentration of H_3PO_4, per cent.	76·27	45·93	40·87	37·17
Oxidation, per cent.	2·1	1·3	1·0	—
Observations	sulphur.	sulphur.	sulphur.	sulphur.
Experiment:	**5.**	**6.**	**7.**	**8.**
Concentration of H_3PO_4, per cent.	34·38	32·83	31·80	20·02
Oxidation, per cent.	—	—	—	—
Observations	Minute amounts.	Very minute deposit.	No deposit.	No deposit.

It is concluded, therefore, that oxidation of ferrous phosphate by sulphur dioxide is just perceptible in a solution containing 332·1 grams of "free" phosphoric acid per litre at 100°.

Discussion of Results.

The reactions of sulphur dioxide with iron phosphates in the presence of concentrated phosphoric acid differ in several ways from those with iron chlorides in concentrated hydrochloric acid solution. In the first place, there is no evidence that sulphur dioxide can act as a reducing agent in the presence of concentrated phosphoric acid, for ferric phosphate, unlike ferric chloride, in the presence of the corresponding concentrated acid, is not affected by the action of sulphur dioxide. The reaction between sulphur dioxide and iron phosphates in concentrated phosphoric acid solution is therefore solely one of oxidation, and may be expressed by the equation

$$4Fe(H_2PO_4)_2 + 4H_3PO_4 + SO_2 = 4Fe(H_2PO_4)_3 + 2H_2O + S.$$

The question now arises as to whether the reaction is a reversible one, like the corresponding ferrous chloride reaction, or whether it proceeds to completion. The fact that mixed ferrous-ferric phosphate solutions gave evidence of oxidation with relatively large percentages of ferric salt rather seems to indicate that the reaction would ultimately proceed to completion. This idea also seems to be supported by the non-reducibility of ferric phosphate by sulphur. Against this conception, however, must be placed the limited yield of ferric salt from an initially pure ferrous phosphate solution and the favourable influence of the concentrated phosphoric acid on the oxidation. Both these facts would be deduced

from the law of mass action if applied to the above equation, taking it as representing a reversible reaction. Undoubtedly, the complicating feature in the reaction is the formation of the stable complex compound which ferric phosphate is known to form with phosphoric acid. This would account for the greater yield of ferric salt from a pure ferrous phosphate solution than from a pure ferrous chloride solution, owing to the fact that the ferric salt formed would be removed from the reaction in the form of the stable complex compound, and hence favour the degree of oxidation. This formation of the complex salt may also account for the non-reducibility of the ferric phosphate in concentrated phosphoric acid solution by the action of sulphur. It is quite conceivable that sulphur may reduce ferric phosphate when not in the form of the complex compound. Such conditions are probably present when sulphur dioxide is passed into a pure ferrous phosphate solution. The sulphur liberated is in a very active state and may react with the ferric phosphate generated before it is taken up in the form of the complex. A consideration of these factors incline the authors to the idea that the reaction of sulphur dioxide with ferrous phosphate is a reversible one similar to that of sulphur dioxide with ferrous chloride in the presence of their corresponding concentrated acids, but that it is modified in the case of the ferrous phosphate by the formation of the complex stable compound which ferric phosphate forms with phosphoric acid.

The facts that sulphur dioxide reduces most readily in a very dilute acid medium, and that it oxidises most readily in a strong acid medium, may be correlated if oxidation and reduction are explained on an ionic basis, oxidation being represented by the surrender of positive charges and reduction by the transference of negative charges.

Sulphur dioxide in aqueous solution is generally regarded as a moderately weak acid ionising principally into $H^{\cdot}$, HSO_3', and SO_3'' ions. It is in this condition that it reacts as a reducing agent. Thus:

$$2Fe^{\cdot\cdot\cdot} + SO_3'' + H_2O = 2Fe^{\cdot\cdot} + SO_4'' + 2H^{\cdot}.$$

In strongly acid solution containing a large number of hydrions, the concentration of SO_3'' ions will be reduced, and, on the above assumption, its power of reducing should be diminished. This is in accordance with experimental results.

Now let it be assumed that sulphur dioxide is capable of ionising to an extremely minute extent as a base, yielding a correspondingly minute amount of sulphur ions. It has been shown that the sulphoxides, the organic analogues of sulphur dioxide, have

basic properties (Fromm and Raiziss, *Annalen*, 1910, **374**, 90; Fromm, *ibid.*, 1913, **396**, 75). This tendency will be all the greater the larger the number of hydrions present in solution. Thus:

$$SO_2 \overset{H_2O}{\rightleftarrows} OS(OH)_2 \rightleftarrows SO'' + 2(OH)',$$

$$SO'' \overset{H_2O}{\rightleftarrows} S'''' + 2(OH)'.$$

In view of the large number of hydrions present in the solution, the concentration of hydroxyl ions would be reduced to a very low value and the reaction towards the right favoured. Oxidation is now represented:

$$S'''' + 4Fe'' \longrightarrow 4Fe''' + S.$$

If oxidation takes place due to the ion SO'',

$$2SO'' + 4Fe'' \longrightarrow 4Fe''' + 2SO,$$
$$2SO + H_2O \longrightarrow H_2S_2O_3,$$

which represents an intermediate stage in the reduction of sulphur dioxide to sulphur. Thiosulphuric acid would break up into sulphur dioxide and sulphur. It may be observed that the latter hypothesis is in many respects a re-statement of the thionyl chloride hypothesis (Wardlaw and Clews, this vol., p. 1103) applied ionically and more generally.

The oxidising properties of arsenic acid, uranyl chloride, permanganic acid, and chromic acids have been explained by Stieglitz ("Qualitative Chemical Analysis," Vol. I, p. 282 *et seq.*) on a similar assumption.

There appears to be room for investigation of these reactions from the point of view of electrical potentials when some of the assumptions made in the above could be tested, and it is hoped that experiments now in progress may throw some further light on this hypothesis.

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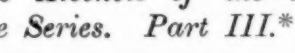
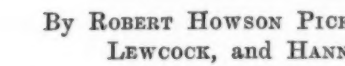
CXXXV.—*The Alcohols of the Hydroaromatic and Terpene Series. Part III.** iso*Pulegol.*

By Robert Howson Pickard, Harold Hunter, William Lewcock, and Hannah Smith de Pennington.

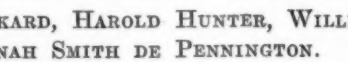
Tiemann and Schmidt (*Ber.*, 1896, **29**, 914) obtained the alcohol *iso*pulegol (II) by the hydrolysis of the condensation product of acetic anhydride and citronellaldehyde (I). The product was so named to distinguish it from the yet unknown isomeric secondary alcohol, which would correspond with the ketone, pulegone (III).



(I.)



(II.)



(III.)

Samples of citronellaldehyde often vary considerably in optical dextrorotatory power, and probably contain the compound,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CHO,$$

as well as that of formula I (see, *inter alia*, Prins, *Chem. Weekblad*, 1917, **14**, 692).

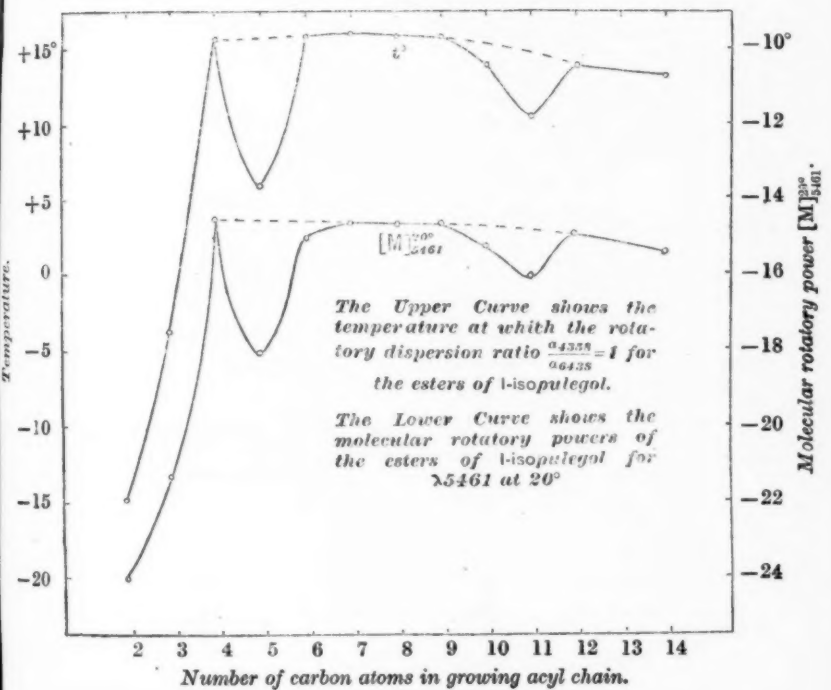
Our preparations of *iso*pulegol from the same sample of aldehyde ($[\alpha]_D^{15°}$ +11·6°) by the method described by Tiemann and Schmidt, or by the modifications of the same proposed by Semmler (*Ber.*, 1909, **42**, 2014) and by Wegscheider and Späth (*Monatsh.*, 1910, **30**, 825), gave *iso*pulegol of rotatory power $[\alpha]_D \pm 2°$. In no case, however, did these products yield, after oxidation with chromic acid, any ketone forming a bisnitroso-derivative so characteristic of pulegone and similar $\alpha\beta$-unsaturated ketones (compare Baeyer and Heinrich, *Ber.*, 1895, **28**, 654). During the condensation, and due to the formation of the *cyclo*hexane ring, two additional carbon atoms become asymmetrical, so that four stereoisomeric pairs of dextro- and lævo-rotatory compounds of the formula ascribed above to *iso*pulegol are theoretically possible. The nomenclature for such isomerides proposed by Aschan, and used in Part II for the menthols, is inconvenient here, as it would necessitate the use of the prefix *iso-* twice over, so the *iso*pulegols may be here simply described as *iso*pulegol, α-, β-, and γ-*iso*pulegols, as it is not yet possible to determine the configurations of the respective isomerides.

A detailed investigation of the mixtures of *iso*pulegols, obtained

* Part I., T., 1907, **91**, 1973. Part II., T., 1912, **101**, 109.

from the condensation of dextrorotatory citronellaldehyde, has now shown that two (and probably not more) of the four possible* isomerides are formed, and as the yield of the *iso*pulegyl acetates rarely amounts to 50 per cent., it is probable that the aldehyde taking part in the condensation is the pure dextrorotatory compound of formula I. The hydrogen phthalic esters of the mixture of alcohols obtained from the condensation product can be separated by the fractional crystallisation of the magnesium † and

FIG. 1.



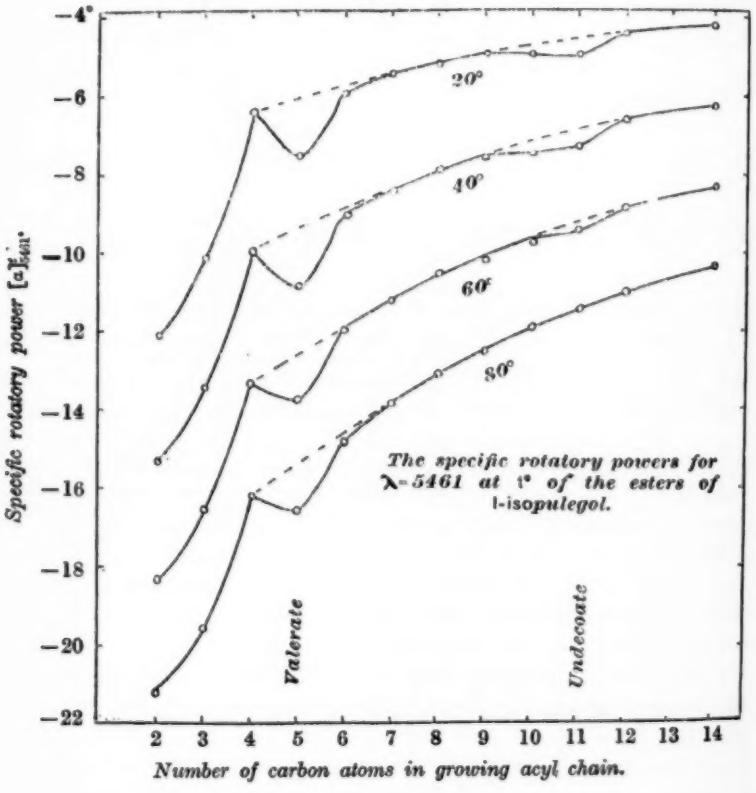
strychnine salts. In this manner, starting from *d*-citronellaldehyde, the esters of *l-iso*pulegol and *d*-α-*iso*pulegol have been isolated, and it has been found that the two alcohols, when reduced, yield respectively *l*-menthol and *d-neo*-menthol, both of which, when oxidised, give *l*-menthone (Part II). The analogy of these cases to that of *d*-borneol and *l-iso*borneol, which, as shown in Part I, both correspond with *d*-camphor, is very striking, whilst Tschugaev (*Ber.*, 1912, **45**, 1293) has shown that tanacetone, when

* That is, assuming no racemisation takes place during the condensation.

† Both magnesium salts are dextrorotatory in ethyl-alcoholic solution.

reduced, forms two tanacetyl alcohols of different configuration and opposite in rotatory power. It would appear that, in general, the reduction of an optically active cyclic ketone to the corresponding secondary alcohol yields a mixture of the two possible *cis*- and *trans*-isomerides of opposite rotatory powers. In this connexion, further analogies may be mentioned, as Aschan has described (*Annalen*, 1901, **316**, 196) the conversion of *d*-camphoric

FIG. 2.

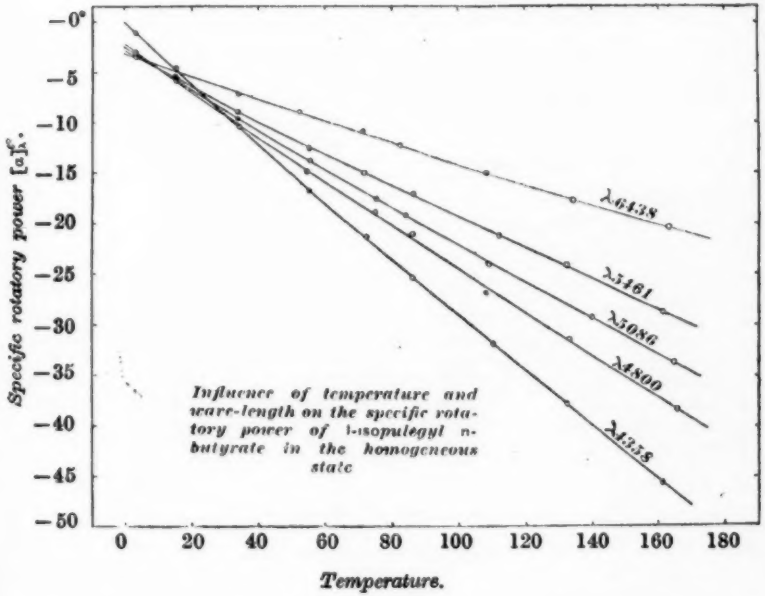


acid (the *cis*-isomeride) into *l-iso*camphoric acid (the *trans*-isomeride), and Forster (T., 1898, **73**, 386) the formation of dextrorotatory bornylamine and lævorotatory *neo*bornylamine from *d*-camphor.

The values obtained for the optical rotatory power for λ 4358 to 6438 of *l-iso*pulegol in the homogeneous state at 20° correspond with a one-term Drude equation almost to within the experimental error, but at higher temperatures they do not. The rotatory

powers of its esters with the normal fatty acids offer a strong contrast to those of the esters of *l*-menthol. Thus in the homologous series their molecular rotatory powers tend to a constant value only at higher temperatures (see table I), and do not in the homogeneous state at any temperature from 10° to 160° agree with a one-term Drude equation, being visibly anomalous in dispersive power at the ordinary temperature (see, for example, Fig. 3). Further, when plotted against molecular weight, the specific rotatory powers, unlike those of the menthyl esters, show

FIG. 3.



maxima (more prominent at the lower temperatures, see Fig. 2) for the valerate and undecoate, that is, when the growing chain may be assumed to return on itself. In ethyl-alcoholic solution there are, in addition, indications of irregularities in such a curve at the propionate and octoate.*

The special positions of the valerate and undecoate on this curve are well illustrated in Fig. 1, which also shows the same phenomenon in the curve drawn to connect molecular weight and the temperatures (extrapolated, where necessary, from observations

* Compare in this connexion somewhat similar phenomena in the rotations of the esters of *d*-1-naphthyl-*n*-hexylcarbinol (Pickard and Kenyon, T., 1914, 105, 2644).

given on p. 1256), at which the esters have a dispersion ratio equal to unity for λ 6438 and 4358. The rotatory powers are given in the tables, but further discussion of these and similar results obtained by one of us and Kenyon (T., 1914, **105**, 830 *et seq.*), or of the criticism by Frankland and Garner (T., 1919, **115**, 639) of the tentative hypothesis adopted to explain them, is postponed until further evidence is available. The variation of the specific rotatory powers of the esters with temperature from 10° to 180° is nearly linear (illustrated in Fig. 3 for the butyrate), and should be considered along with similar results obtained by Kenyon (T., 1914, **105**, 2226) in view of the suggestions of Patterson (T., 1913, **103**, 156).

TABLE I.

Molecular Rotatory Powers of l-iso*Pulegol and its Esters in the Homogeneous State.*

	$[M]^{20°}_{6438}$.	$[M]^{90°}_{6438}$.	$[M]^{20°}_{4358}$.	$[M]^{80°}_{4358}$.
*l-iso*Pulegol.....	−28·1°	−29·9°	−66·3°	−72·2°
Acetate	18·8	31·0	30·7	61·9
Propionate	17·2	30·1	25·6	61·0
n-Butyrate	12·4	26·6	14·1	52·4
n-Valerate	14·9	29·0	20·5	57·4
n-Hexoate	13·1	27·9	14·7	54·1
n-Heptoate	12·9	27·1	14·6	53·2
n-Octoate	12·9	27·4	14·7	53·4
n-Nonoate	12·8	27·1	14·5	53·3
n-Decoate	12·8	27·8	15·9	53·5
n-Undecoate	13·9	27·8	17·8	53·0
n-Dodecoate	12·9	27·9	15·6	53·5
Myristate	13·9	28·4	16·3	54·7

EXPERIMENTAL.

Isolation of l-iso*Pulegol.*

The mixture (b. p. 82—90°/10 mm.) of alcohols (obtained by the hydrolysis of the condensation product of citronellaldehyde, $[\alpha]_D$ +11·6°, and acetic anhydride) is heated in an oil-bath at 110° for twelve hours with an equimolecular amount of phthalic anhydride. The product is dissolved in a very dilute cold aqueous solution of sodium carbonate, which is then carefully extracted with ether to remove neutral compounds. Any dissolved ether is removed by a current of air, and then the solution precipitated with the calculated amount of a solution of magnesium chloride. The resulting pasty mass is strained off and crystallised eight times from alcohol containing some water, which is diminished as the separation nears completion. By working up the mother liquors (*a*) by concentration of the alcoholic solutions, and (*b*) by recovery

of the hydrogen phthalic esters from the more soluble fractions and re-working these as before, a yield of just over 40 per cent. of the magnesium salt of *l-iso*pulegyl hydrogen phthalate is obtained.

Magnesium l-iso*pulegyl phthalate* crystallises from aqueous alcohol in lustrous flakes with $6H_2O$ (Found: Mg = 3·3; H_2O = 14·3. $C_{36}H_{42}O_8Mg,6H_2O$ requires Mg = 3·3; H_2O = 14·6 per cent.), which melt at 111° and are soluble in chloroform or acetone. It has $[\alpha]_{6438}$ +7·8°, $[\alpha]_{5893}$ +18·2°, $[\alpha]_{5461}$ +23·2°, $[\alpha]_{5086}$ +30·3°, and $[\alpha]_{4358}$ +57·4° in alcohol (c = 5) at 20°. It is decomposed by cold hydrochloric acid, which precipitates l-iso*pulegyl hydrogen phthalate*. This ester crystallises from glacial acetic acid in stout prisms, which melt at 106°. It has $[\alpha]_{6438}$ −19·39°, −25·77°; $[\alpha]_{5893}$ −23·55°, −31·91°; $[\alpha]_{5461}$ −28·59°, −39·10°; $[\alpha]_{5086}$ −33·44°, −37·55°; and $[\alpha]_{4358}$ −53·32° and −75·58° in alcohol and benzene respectively (c = 5) at the temperature of the laboratory.

The *strychnine* salt crystallises from absolute alcohol in long, prismatic needles, which melt at 205°. The homogeneity of the ester was inferred from the constancy of its lævorotation in alcohol and chloroform (i) after an attempted fractional crystallisation from acetic acid, and (ii) after conversion into the strychnine salt, which was repeatedly recrystallised, and its recovery.

l-iso*Pulegol* is obtained by the hydrolysis of the hydrogen phthalate with an excess of sodium hydroxide dissolved in ethyl alcohol. It boils at 88°/10 mm., and its rotatory power is unaltered by partial esterification with either phthalic or acetic anhydride, the unesterified *iso*pulegol and that obtained from the hydrolysis of the esters having identical rotations. When suspended in water containing 10 per cent. of gum arabic in the presence of colloidal palladium, it is reduced rapidly by hydrogen to a crystalline solid (m. p. 42° and $[\alpha]_D^{47°}$ −49·4°) identical with *l*-menthol.

d-α-iso*Pulegol*.—The more soluble component obtained in the separation as described above of the magnesium salt of *l-iso*pulegyl hydrogen phthalate remains after the removal of the alcohol as a pasty mass, which is strongly dextrorotatory in ethyl-alcoholic solution. The mixture of hydrogen phthalates is recovered from the magnesium salts, has a specific rotatory power about ±0°, and by careful fractional crystallisation from acetic acid can be further separated, the most soluble fraction having $[\alpha]_D$ about +8° in 5 per cent. ethyl-alcoholic solution. This dextrorotatory ester was dissolved in the calculated amount of a dilute solution of sodium carbonate and fractionally precipitated by small amounts of magnesium chloride solution. After repeating the process ten times,

the most soluble magnesium salt yielded a hydrogen phthalate which had $[\alpha]_D + 30{\cdot}1°$ in ethyl alcohol ($c = 5$), and solidified in flat prisms melting at 117°. When hydrolysed, it yielded a dextrorotatory *α-iso*pulegol (still containing, apparently, about 10 per cent. of *l-iso*pulegol), which had $D^{19{\cdot}5°}_{4°}$ 0·9172, $[\alpha]^{19{\cdot}5°}_{D} + 29{\cdot}3°$, $[\alpha]^{19{\cdot}5°}_{5461} + 34{\cdot}5°$, and $[\alpha]^{19{\cdot}5°}_{4358} + 54{\cdot}9°$.

When reduced by hydrogen in the presence of colloidal palladium, it gave an impure *d-neo*menthol with $[\alpha]^{19°}_{5461} + 10{\cdot}92°$, which yielded a hydrogen succinate melting at 68° after two crystallisations from light petroleum, whereas the *l-neo*menthol described in Part II (*loc. cit.*) had $[\alpha]^{18°}_{5461} - 21{\cdot}32°$, and gave a hydrogen succinate melting at 67—68°. The amount of material available did not permit of a further repetition of the exceedingly tedious process of separation. The *iso*pulegones obtained from *l-iso*pulegol, and the impure *d-α-iso*pulegol by oxidation with chromic acid at 50° gave identical lævorotatory oximes (m. p. 121°, and volatile in steam) and semicarbazones (m. p. 171°).

Esters of l-iso*Pulegol and Normal Aliphatic Acids.*

The esters were prepared by the action of the requisite acid chlorides on a solution of *iso*pulegol in pyridine, except in the case of the acetate, propionate, valerate, and heptoate, where the acid anhydrides were employed. All are fragrant, limpid liquids at the ordinary temperature. Samples of *iso*pulegol recovered from the esterification process, and also from the esters after these had undergone polarimetric examination, were unaltered in rotatory power. Two samples of *iso*pulegyl valerate were also prepared by fractional esterification of the alcohol, and were identical in rotatory power.

In table II are given some of their physical properties, in table III the results of the determinations of their density ($D^{t°}_{4°}$), and negative rotatory power ($\alpha^{100\text{ mm.}}$), the second set of figures for the compounds being the resulting calculated values at the temperature named of the specific rotatory power, and in table IV the data of determinations of rotatory power in ethyl alcohol.

The densities were determined in a pyknometer holding about 1·5 c.c., except in the case of *iso*pulegol, its acetate and propionate, when one holding 4 c.c. was used.

The rotations were measured in tubes of 50 mm. length, round which cooled water or heated mineral oil was circulated by means of a pump, but are here given as for 100 mm.

TABLE II.

l-iso*Pulegol and its Esters.*

	Boiling point °C./mm.	$D_{4^\circ}^{18^\circ}$.	$n_{4^\circ}^{18^\circ}$.	Molecular refractive power.* $\frac{n^2-1}{n^2+2}\cdot\frac{M}{d}$ observed.	Molecular refractive power.* Difference from calculated value.	Refractive dispersive power † $n_{4358}^{18^\circ}-n_{6438}^{18^\circ}$.
*l-iso*Pulegol	94°/14	0·9110 (at 20°)	1·4723 (at 20°)	47·41	+0·25	0·01464
Acetate	103°/14	0·9350	1·4565	57·08	0·52	0·01402
Propionate	91°/4	0·9300	1·4558	61·41	0·26	0·01367
n-Butyrate	116°/5	0·9245	1·4563	65·96	0·21	0·01361
n-Valerate	119°/4	0·9185	1·4578	70·73	0·38	0·01350
n-Hexoate	153°/13	0·9150	1·4581	75·21	0·25	0·01343
n-Heptoate	134°/3	0·9113	1·4588	79·83	0·27	0·01353
n-Octoate	159°/5	0·9065	1·4584	84·42	0·26	0·01342
n-Nonoate	161°/6	0·9053	1·4601	89·04	0·27	0·01334
n-Decoate	158°/2	0·9020	1·4603	93·65	0·28	0·01334
n-Undecoate	164°/2	0·8969	1·4614	98·46	0·48	0·01329
n-Dodecoate	188°/3	0·8969	1·4621	103·10	0·52	0·01331
Myristate	189°/2	0·8933 (at 20°)	1·4618 (at 20°)	112·10	0·31	0·01331

* The structure of the *iso*pulegyl ring causes an increment of about 0·25 above the ordinary calculated value of the molecular refraction according to the Lorentz and Lorenz formula. It has often been observed (see Pickard and Kenyon, *loc. cit.*) that the members of homologous series containing five and eleven atoms in the growing chain have molecular refractions which differ from the calculated values by small amounts just greater than the experimental error.

† These values when plotted against molecular weight lie approximately on a continuous curve, becoming constant at about the ninth member of the series.

Table III.

l-iso*Pulegol*.

Temp.	18·4°	36·5°	70·5°	98·5°	131°	172°
D_4^t	0·9123	0·8962	0·8661	0·8415	0·8134	0·7764
Temp.	15·5°	57·5°	105°	147°	163°	
α_{6438}	16·60	16·61	16·66	16·72	16·74	
Temp.	15·5°	56·5°	93·5°	141·5°	168°	
α_{5461}	23·60	23·74	23·70	23·82	23·98	
Temp.	15·5°	57°	101·5°	148°	165°	
α_{5086}	27·64	27·76	27·86	28·22	28·38	
Temp.	15·5°	56·5°	105·5°	150°	166·5°	
α_{4800}	31·46	31·78	32·36	32·80	32·98	
Temp.	15·5°	56·5°	103·5°	147°		
α_{4358}	39·20	39·86	40·52	41·38		

Temp.	20°	40°	60°	80°	100°	120°	140°	160°
$[\alpha]_{6438}^t$	18·23	18·61	18·98	19·39	19·83	20·26	20·73	21·22
$[\alpha]_{5461}^t$	25·90	26·46	27·05	27·65	28·28	28·95	29·66	30·38
$[\alpha]_{5086}^t$	30·31	31·01	31·74	32·47	33·25	34·08	34·95	35·83
$[\alpha]_{4800}^t$	34·51	35·43	36·37	37·35	38·37	39·45	40·57	41·74
$[\alpha]_{4358}^t$	43·07	44·30	45·55	46·86	48·22	49·67	51·16	52·71

l-iso*Pulegyl Acetate*.

Temp.	16·1°	41·4°	84·1°	131·9°		
D_4^t	0·9364	0·9149	0·8794	0·8359		
Temp.	5·5°	21°	41°	66·5°	82°	
α_{6438}	7·54	9·10	10·62	12·84	14·14	
Temp.	0·5°	5·5°	21°	41°	64·5°	84°
α_{5461}	8·78	9·40	11·56	14·18	17·06	19·12
Temp.	5·5°	21°	41°	65°	81·5°	
α_{5086}	10·16	12·92	15·90	19·40	21·54	
Temp.	5·5°	21°	41°	65·5°	84·5°	
α_{4800}	10·74	13·80	17·34	21·48	24·48	
Temp.	0°	5·5°	21°	41°	64·5°	83°
α_{4358}	9·48	10·98	14·82	19·70	24·70	28·56

Temp.	20°	40°	60°	80°
$[\alpha]_{6438}^t$	9·58	11·61	13·65	15·82
$[\alpha]_{5461}^t$	12·22	15·32	18·34	21·23
$[\alpha]_{5086}^t$	13·61	17·18	20·74	24·16
$[\alpha]_{4800}^t$	14·57	18·71	22·83	26·95
$[\alpha]_{4358}^t$	15·65	21·24	26·38	31·56

TABLE III. (*continued*).

l-iso*Pulegyl Propionate*.

Temp.	12·2°	16·3°	44·6°	56·4°	82·6°	89·6°	131·3°
D_4^t	0·9346	0·9315	0·9084	0·8987	0·8771	0·8721	0·8337
Temp.	3°		21·8°	46°	67°		84·5°
α_{6438}	5·74		7·78	9·82	11·44		13·02
Temp.	2°		21·8°	45°	67°		85°
α_{5461}	6·80		9·64	13·08	15·58		17·88
Temp.	2·5°		21·8°	46°	67°		84·5°
α_{5086}	7·02		10·68	14·46	17·62		20·18
Temp.	2°		21·8°	45·5°	67°		84·5°
α_{4800}	7·20		11·14	15·80	19·38		22·50
Temp.	2°		21·8°	45°	67·5°		85°
α_{4358}	6·66		11·86	17·66	22·76		26·64
Temp.	20°		40°	60°	80°		
$[\alpha]^t_{6438}$	8·19		10·17	12·22	14·33		
$[\alpha]^t_{5461}$	10·13		13·49	16·58	19·63		
$[\alpha]^t_{5086}$	11·06		14·80	18·51	22·21		
$[\alpha]^t_{4800}$	11·63		16·12	20·36	24·68		
$[\alpha]^t_{4358}$	12·2 0		17·98	23·54	29·04		

l-iso*Pulegyl* n-*Butyrate*.

Temp.	20°	43·5°	54°	72°	113°	131°	147°		
D_4^t	0·9230	0·9046	0·8965	0·8822	0·8451	0·8293	0·8137		
Temp.	3°	15°	34°	52°	71°	82°	108°	134°	163°
α_{6438}	3·20	4·50	6·46	8·08	9·70	10·76	12·76	14·68	16·30
Temp.	3°	15°	34°	55°	71·5°	86°	112°	132°	161°
α_{5461}	3·10	5·02	8·20	11·20	13·26	14·88	18·08	19·96	23·00
Temp.	3°	15°	34°	55°	75°	84°	109°	140°	164°
α_{5086}	2·90	5·60	8·82	12·28	15·36	16·66	20·50	24·00	26·80
Temp.	3°	15°	34°	54°	75°	86°	108°	133°	165°
α_{4800}	2·78	5·34	9·42	13·40	16·62	18·28	22·96	25·90	30·54
Temp.	3°	15°	34°	55°	72°	86°	110°	132°	161°
α_{4358}	1·00	4·32	9·52	14·98	18·84	22·04	27·12	31·28	36·52
Temp.	20°	40°	60°	80°	100°	120°	140°	160°	
$[\alpha]^t_{6438}$	5·53	7·78	9·87	11·87	14·12	16·31	18·21	20·12	
$[\alpha]^t_{5461}$	6·46	9·99	13·32	16·24	19·39	22·40	25·54	28·60	
$[\alpha]^t_{5086}$	7·02	10·98	14·69	18·35	22·41	26·00	29·34	32·77	
$[\alpha]^t_{4800}$	6·93	11·77	16·13	19·88	24·65	28·77	32·96	37·20	
$[\alpha]^t_{4358}$	6·28	12·34	18·10	23·41	29·09	34·59	39·86	45·24	

TABLE III. (*continued*).

l-iso*Pulegyl* n-*Valerate*.

Temp.	22°	30°	56·5°	68·5°	75°	87°	127°
D_4^t	0·9159	0·9095	0·8882	0·8787	0·8735	0·8630	0·8264
Temp.	2°	14·5°	16°	41°	51·5°	61°	87°
α_{6438}	3·74	5·24	5·36	7·64	8·54	9·20	11·06
Temp.	2°	15°	16°	41°	51°	60·5°	87°
α_{5461}	4·10	6·24	6·32	9·98	11·14	12·20	15·16
Temp.	2°	15°	16°	41°	51·5°	61°	87°
α_{5086}	4·26	6·78	6·88	10·90	12·54	13·80	17·20
Temp.	1·5°	15°	16°	41°	51°	60°	87°
α_{4800}	4·12	6·92	7·02	11·66	13·72	15·28	19·20
Temp.	0·5°	15°	16°	41°	51·5°	60°	87·5°
α_{4358}	3·02	6·66	6·78	12·92	15·38	17·14	22·32

Temp.	20°	40°	60°	80°
$[\alpha]^t_{6438}$	6·28	8·39	10·32	12·19
$[\alpha]^t_{5461}$	7·57	10·87	13·78	16·51
$[\alpha]^t_{5086}$	8·28	11·99	15·47	18·79
$[\alpha]^t_{4800}$	8·57	12·87	17·12	20·95
$[\alpha]^t_{4358}$	8·63	14·16	19·36	24·11

l-iso*Pulegyl* n-*Hexoate*.

Temp.	14·6°	32·8°	42°		55·2°
D_4^t	0·9187	0·9040	0·8972		0·8870
Temp.	6°	14·5°	40·5°	68°	83·5°
α_{6438}	3·32	4·14	6·76	8·84	9·84
Temp.	6·5°	15°	41·5°	68°	84·5°
α_{5461}	3·62	4·54	8·38	11·44	13·42
Temp.	6°	14·5°	41·5°	68°	83·5°
α_{5086}	3·44	4·72	9·10	12·92	15·02
Temp.	6·5°	15°	41°	68°	84°
α_{4800}	3·12	4·84	9·62	14·18	16·54
Temp.	6·5°	15°	42°	68°	80·5°
α_{4358}	1·94	4·16	10·82	16·28	18·70

Temp.	20°	40°	60°	80°
$[\alpha]^t_{6438}$	5·19	7·45	9·33	11·06
$[\alpha]^t_{5461}$	5·95	9·04	11·93	14·86
$[\alpha]^t_{5086}$	6·19	9·84	13·31	16·77
$[\alpha]^t_{4800}$	6·30	10·46	14·55	18·41
$[\alpha]^t_{4358}$	5·84	11·46	16·66	21·47

TABLE III. (*continued*).

l-iso*Pulegyl* n-*Heptoate*.

Temp.	18°	39·5°	60°	96°		
D_4^t	0·9111	0·8946	0·8802	0·8522		
Temp.	5·5°	21·5°	33·5°	44°	66·5°	83°
α_{6438}	3·08	4·48	5·54	6·22	7·90	9·08
Temp.	6·5°	21·5°	33·5°	44°	66°	87°
α_{5461}	3·20	5·10	6·66	8·04	10·56	12·76
Temp.	5·5°	21·5°	34°	40°	65·5°	84°
α_{5086}	2·92	5·42	7·56	8·56	11·72	14·06
Temp.	6·5°	21·5°	34°	44°	66°	85°
α_{4800}	2·70	5·56	8·00	9·64	13·12	15·84
Temp.	7°	21·5°	33·5°	44°	65·5°	87°
α_{4358}	1·82	5·28	8·16	10·44	14·54	18·74
Temp.	20°		40°	60°		80°
$[\alpha]^t_{6438}$	4·84		6·71	8·43		10·17
$[\alpha]^t_{5461}$	5·48		8·45	11·27		13·88
$[\alpha]^t_{5086}$	5·76		9·44	12·57		15·68
$[\alpha]^t_{4800}$	5·83		10·07	13·82		17·53
$[\alpha]^t_{4358}$	5·50		10·74	15·41		20·00

l-iso*Pulegyl* n-*Octoate*.

Temp.	19°		23°		38°		52·5°
D_4^t	0·9055		0·9028		0·8925		0·8826
Temp.	3°	17·3°	42°	45°	62°	76·5°	82°
α_{6438}	2·40	3·90	6·06	6·24	7·32	8·28	8·56
Temp.	3·5°	17·3°	37°	42°	63°	68·5°	86·5°
α_{5461}	2·64	4·36	6·74	7·30	9·54	10·12	11·90
Temp.	3°		15°	41·5°	67·5°		85·5°
α_{5086}	2·44		4·50	8·10	11·30		13·32
Temp.	3°	17·3°	41·5°	61°	67°		84°
α_{4800}	2·00	4·78	8·86	11·76	12·56		14·90
Temp.	3·5°	17·3°	37°	43·5°	60°		71·5°
α_{4358}	0·74	4·08	8·36	9·70	13·08		15·06
Temp.	20°		40°	60°		80°	
$[\alpha]^t_{6438}$	4·60		6·58	8·28		9·78	
$[\alpha]^t_{5461}$	5·23		7·92	10·52		13·09	
$[\alpha]^t_{5086}$	5·68		8·84	11·88		14·84	
$[\alpha]^t_{4800}$	5·86		9·68	13·23		16·69	
$[\alpha]^t_{4358}$	5·26		10·10	14·82		19·07	

TABLE III. (*continued*).

l-iso*Pulegyl* n-*Nonoate*.

Temp.		19·3°	36°	57·4°	
D_4^t		0·9042	0·8925	0·8768	
Temp.	4°	23·5°	49·5°	64·5°	81·5°
α_{6438}	2·58	4·26	6·18	6·94	8·00
Temp.	4·5°	23·5°	47°	63°	82·5°
α_{5461}	2·44	4·94	7·58	9·34	10·98
Temp.	4°	23°	49°	81·5°	
α_{5086}	2·42	5·34	8·64	12·22	
Temp.	4°	23·5°	48°	81·5°	
α_{4800}	2·30	5·52	9·34	13·54	
Temp.	4·5°	23·5°	46°	63°	82°
α_{4358}	1·16	5·14	9·68	12·72	15·94
Temp.	20°	40°	60°	80°	
$[\alpha]^t_{6438}$	4·36	6·20	7·72	9·20	
$[\alpha]^t_{5461}$	4·98	7·64	10·24	12·57	
$[\alpha]^t_{5086}$	5·38	8·43	11·39	14·06	
$[\alpha]^t_{4800}$	5·51	9·22	12·64	15·62	
$[\alpha]^t_{4358}$	4·94	9·47	13·94	18·12	

l-iso*Pulegyl* n-*Decoate*.

Temp.	17°		45·5°		65°			84°	
D_4^t	0·9028		0·8821		0·8684			0·8545	
Temp.	1°	14°	44°	60°	77°	98°	119°	141·5°	170°
α_{6438}	2·50	3·32	5·46	6·44	7·62	8·50	10·16	11·22	12·50
Temp.	3°	14°	42°	59°	77°	94·5°	118°	141·5°	168°
α_{5461}	2·30	3·70	6·90	8·32	10·10	11·34	13·28	15·00	16·86
Temp.	1°	14°	42°	59°	78°	95°	120°	140·5°	170°
α_{5086}	1·90	3·80	7·46	9·64	11·56	13·30	15·56	17·40	19·98
Temp.	1°	14°	41°	58°	79°	95°	121°	140·5°	170°
α_{4800}	1·96	3·90	7·88	10·38	12·98	14·74	17·72	19·74	22·86
Temp.	3°	14°	42°	58°	77°	94·5°	117·5°	141°	166·5°
α_{4358}	0·58	3·38	8·94	11·48	14·48	16·86	20·22	23·46	26·22
Temp.	20°		40°		60°			80°	
$[\alpha]^t_{6438}$	4·15		5·78		7·41			9·02	
$[\alpha]^t_{5461}$	4·93		7·52		9·75			11·92	
$[\alpha]^t_{5086}$	5·20		8·19		11·10			13·69	
$[\alpha]^t_{4800}$	5·35		8·71		12·23			15·20	
$[\alpha]^t_{4358}$	5·15		9·66		13·54			17·38	

TABLE III. (*continued*).

l-iso*Pulegyl* n-*Undecoate*.

Temp.	17°	55°	88·5°		131°
D_4^t	0·8972	0·8715	0·8475		0·8138
Temp.	3·5°	15·5°	38·5°	56°	88°
α_{6438}	2·58	3·42	5·16	6·12	7·74
Temp.	2°	15·5°	38·5°	56°	88·5°
α_{5461}	2·46	3·96	6·28	7·96	10·38
Temp.	4°	15°	38·5°	55·5°	90°
α_{5086}	2·70	4·00	7·10	9·06	11·86
Temp.	4·5°	15·5°	39°	55·5°	91°
α_{4800}	2·56	4·22	7·78	9·74	13·46

Temp.*	2·5°	15·5°	37·5°	53°	68·5°	87°
α_{4358}	1·48	4·18	7·90	10·34	12·42	15·02

Temp.	20°	40°	60°	80°
$[\alpha]^t_{6438}$	4·31	5·94	7·31	8·65
$[\alpha]^t_{5461}$	4·98	7·35	9·48	11·48
$[\alpha]^t_{5086}$	5·29	8·21	10·83	13·02
$[\alpha]^t_{4800}$	5·54	8·94	11·82	14·52
$[\alpha]^t_{4358}$	5·54	9·41	13·18	16·44

l-iso*Pulegyl* n-*Dodecoate*.

Temp.	14°	20°	43°	58·5°	80°
D_4^t	0·8996	0·8959	0·8794	0·8684	0·8540
Temp.	4°	17·5°	39°	56°	81°
α_{6438}	2·44	3·30	4·64	5·78	7·14
Temp.	4·5°	17°	40°	57°	80°
α_{5461}	2·40	3·66	5·90	7·48	9·40
Temp.	4°	18°	38°	55°	81°
α_{5086}	2·36	4·10	6·46	8·34	10·70
Temp.	4°	18°	38°	55°	81°
α_{4800}	2·10	4·16	7·00	9·12	11·82

Temp.	4·5°	17·5°	38°	53°	69·8°	82°
α_{4358}	1·44	3·52	7·26	9·58	12·08	13·90

Temp.	20°	40°	60°	80°
$[\alpha]^t_{6438}$	3·84	5·35	6·89	8·32
$[\alpha]^t_{5461}$	4·42	6·69	8·88	11·01
$[\alpha]^t_{5086}$	4·83	7·60	10·14	12·47
$[\alpha]^t_{4800}$	4·98	8·23	11·18	13·75
$[\alpha]^t_{4358}$	4·65	8·57	12·27	15·93

TABLE III. (*continue...*).

l-iso*Pulegyl Myristate.*

Temp.		12·4°	34·8°	54·8°	
D^t_4		0·8985	0·8832	0·8693	
Temp.	5°	22°	43°	65·5°	84·5°
α_{6438}	2·44	3·54	4·84	6·00	6·82
Temp.	5°	22°	43°	65°	83·5°
α_{5461}	2·40	3·96	5·86	7·62	9·10
Temp.	5°	22°	43°	65·5°	84°
α_{5086}	2·52	4·44	6·54	8·54	10·36
Temp.	5°	22°	43°	65·5°	83·5°
α_{4800}	2·42	4·58	7·08	9·26	11·44
Temp.	4·5°	22°	43°	65°	84°
α_{4358}	1·66	4·26	7·58	10·56	13·36
Temp.	20°	40°	60°	80°	
$[\alpha]^t_{6438}$	3·81	5·30	6·63	7·82	
$[\alpha]^t_{5461}$	4·23	6·30	8·32	10·33	
$[\alpha]^t_{5086}$	4·68	7·05	9·38	11·69	
$[\alpha]^t_{4800}$	4·84	7·62	10·28	13·00	
$[\alpha]^t_{4358}$	4·48	8·07	11·44	15·02	

Some of the materials used in this work were purchased from a grant made by the Government Committee of the Royal Society; the receipt of a personal grant from the Department of Scientific and Industrial Research to one of the authors is acknowledged, whilst the authors' thanks are also due to Messrs. Schimmel, of Leipzig, for a pre-war gift of crude *iso*pulegyl acetate.

TABLE IV.

Determinations of Rotatory Power in (approx.) 5 per cent. Solution in Ethyl Alcohol.

Ester.	Length of tube. Cm.	Weight of solute. Grams.	α_{6438}.	α_{5461}.	α_{5086}.	α_{4800}.	α_{4358}.	$[\alpha]^{20°}_{6438}$.	$[\alpha]^{20°}_{5461}$.	$[\alpha]^{20°}_{5086}$	$[\alpha]^{20°}_{4800}$.	$[\alpha]^{20°}_{4358}$.
*l-iso*Pulegyl Acetate	20	1·0020	1·67	2·07	2·40	2·66	2·95	16·66	20·66	23·95	26·55	29·44
Propionate...	20	0·9926	1·57	1·95	2·27	2·49	2·75	15·81	19·64	22·87	25·08	27·70
n-Butyrate...	20	1·0060	1·42	1·66	1·93	2·08	2·37	14·11	16·50	19·19	20·67	23·56
n-Valerate ...	20	0·9944	1·42	1·67	1·96	2·15	2·40	14·28	16·79	19·71	21·62	24·13
n-Hexoate ...	20	0·8353	0·95	1·20	1·43	1·57	1·76	11·37	14·36	17·12	18·79	21·07
n-Heptoate...	20	0·9988	1·08	1·38	1·59	1·71	1·98	10·81	13·82	15·92	17·12	19·83
n-Octoate ...	20	0·9996	1·03	1·35	1·51	1·63	1·92	10·30	13·50	15·10	16·81	19·21
n-Nonoate ...	20	0·9990	1·02	1·30	1·48	1·63	1·87	10·21	13·01	14·81	16·31	18·72
n Decoate ...	20	1·0030	0·98	1·25	1·42	1·57	1·76	9·77	12·47	14·16	15·65	17·55
n-Undecoate	20	0·9940	0·98	1·18	1·36	1·53	1·63	9·86	11·87	13·68	15·39	16·40
n-Dodecoate	20	1·0175	0·96	1·21	1·38	1·53	1·68	9·44	11·90	13·56	15·04	16·51
Myristate ...	20	0·9957	0·92	1·09	1·27	1·41	1·54	9·24	10·95	12·76	14·16	15·46

All solutions for the observations of rotatory power recorded above were prepared by making up about 1 gram of the substance to 20 c.c., with alcohol at 20°, at which temperature all observations were also made.

BATTERSEA POLYTECHNIC.

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CXXXVI.—*Some New Azopyrazolones and Allied Compounds.*

By Kenneth Herbert Saunders.

In seeking to ascertain the effect produced on the colour of compounds of the azo-type belonging to the benzene, naphthalene, and anthraquinone groups by increasing molecular weight by a comparison of the absorption spectra of the various members, it was found that scarcely any of the required substances beyond the benzeneazo- and naphthaleneazo-series have been prepared. Although azobenzene and the azonaphthalenes are very well known, α-azoanthraquinone has only been discovered in recent years (Gattermann and Ebert, *Ber.*, 1916, **49**, 2117), whilst the azoanthracenes are unknown. For the purpose of such a comparison, the azopyrazolones, being more strongly coloured and much faster to light than the corresponding members of the azobenzene series, would seem to be more suitable, and have therefore been selected for the investigation. A complete series of compounds has been prepared in which the anthraquinone nucleus is introduced either into the 1-position of the pyrazolone ring or as the first component of an azopyrazolone compound, or in both positions together.

The 1-anthraquinonylpyrazolones cannot be obtained by the simple process of heating ethyl acetoacetate with the required hydrazine, because reaction invariably stops with the formation of the hydrazone. The further action of condensing agents is necessary before the β-anthraquinonylhydrazone of ethyl acetoacetate can be converted into a pyrazolone. Although boiling sulphuric acid will effect this change in one stage, the yield of the pyrazolone is small, a large proportion of the original hydrazine being regenerated. A far more satisfactory method is to boil the hydrazone with acetic anhydride, whereby 1-β-anthraquinonyl-5-acetyl-3-methylpyrazolone is produced (Möhlau and Reiner, *Ber.*, 1912, **45**, 2244), and then hydrolyse with hydrochloric acid. 1-*β-Anthraquinonyl*-3-*methyl*-5-*pyrazolone* is obtained in this way as an orange powder showing all the properties of the class except that the anthraquinone nucleus causes it to be highly insoluble and rather slow to enter into reaction. It couples with diazonium salts in acetic acid solution to give typical arylazopyrazolones of great stability, which do not show definite melting points, but slowly begin to decompose above 250° or thereabout.

The sole product of the complete condensation of the α-anthra-

quinonylhydrazone of ethyl acetoacetate is pyrazoleanthrone, and the required pyrazolone cannot be obtained (Reiner, *Diss.*, Dresden, 1912; Möhlau and Viertel, *Ber.*, 1912, **45**, 3238). Difficulty in obtaining the α-isomeride is also experienced in the preparation of the 1-naphthyl-5-pyrazolones (Knorr, *Ber.*, 1884, **17**, 550), for whilst 1-β-naphthyl-5-pyrazolone is easily produced, the product obtained from the fusion of α-naphthylhydrazine with ethyl acetoacetate contains scarcely any pyrazolone, whilst in solvents the condensation does not take place at all. As noted above, the colour of β-anthraquinonylpyrazolone is orange, although all the other pyrazolones of this type hitherto described are colourless. The colour vibration may be set up by the carbonyl group of the pyrazolone reacting with that of the anthraquinone nucleus, owing to their being so arranged in space that they are in the closest proximity. That the colour is concerned with these two groups is shown by the fact that acetylation of the pyrazolone changes the colour to lemon-yellow. It seems possible, therefore, that the colour of the products, and also the difficulty of introducing the α-anthraquinonyl group, may be referred to the contiguous position of the carbonyl groups in the anthraquinone and pyrazolone nuclei. Evidence for this view would be the preparation of the 1-α-naphthyl- and 1-α-anthraquinonyl-3-pyrazolone, but these compounds do not yet seem to have been described.

For the preparation of the arylazo-derivatives of the above anthraquinonylpyrazolone, the alternative process, due to Bülow and Hecking (*Ber.*, 1911, **44**, 437), has also been investigated. The first two steps are easily accomplished, β-anthraquinonediazonium sulphate, for example, readily combining with ethyl acetoacetate, whilst the azo-compound so formed, on boiling with hydroxylamine, passes into the *iso*oxazolone. When, however, the *iso*oxazolone is treated with hydrazines, although a yield approaching theoretical is obtained from hydrazine itself, the yield steadily falls as phenyl, naphthyl, and anthraquinonyl nuclei are introduced, so that the method is useless for producing the higher members of the series.

Sodium dihydroxytartrate decomposes below a temperature at which β-anthraquinonylhydrazine will react, excepting with extreme slowness, so that it was found impossible to obtain new members of the tartrazine group by this method, all products of reaction from a large variety of solvents being for the most part a mixture of the decomposition products of the dihydroxytartrate.

The anthraquinoneazopyrazolones, whether unsubstituted in the 1-position or substituted by phenyl, naphthyl, or anthraquinonyl residues, are characterised by having, at best, only a sparing solu-

bility in most organic solvents. They can be crystallised fairly well from pyridine or nitrobenzene. They also have the property of many anthraquinoneazo-compounds of dissolving in warm alkali hydroxide to form a deep purple solution, and, in the case of *4-β-anthraquinoneazo-3-methyl-5-pyrazolone*, which is very readily soluble in this reagent, a monosodium salt can be crystallised by salting the warm solution. Their melting points are very high, so that often decomposition sets in before fusion takes place.

The property which first attracted attention to the group is that 4-β-anthraquinoneazo-1-phenyl-3-methyl-5-pyrazolone can exist in two differently coloured modifications: (1) yellow, unstable, and (2) red, stable (Möhlau and Reiner, *Ber.*, 1912, **45**, 2240). These authors prepared both forms, and found that the same absorption spectrum is given by both, and that, on heating, the yellow form changes into the red without melting. The same behaviour is shown by *4-β-anthraquinoneazo-1-β-naphthyl-3-methyl-5-pyrazolone*, excepting that the yellow form is still less stable, and only appears directly after combination has taken place, rapidly changing to the red form on warming. On the other hand, 4-β-anthraquinoneazo-3-methyl-5-pyrazolone and *4-β-anthraquinoneazo-1-β-anthraquinonyl-3-methyl-5-pyrazolone* exist in the solid state only in yellow forms, and by no means can be induced to crystallise otherwise. It would appear, therefore, that a phenyl, and more particularly a naphthyl, nucleus substituting the 1-position of the pyrazolone ring causes the ordinary yellow form to be unstable, with the result that slight rearrangement takes place on crystallisation, a more stable, red form being produced.

The colour of the solutions of the anthraquinoneazopyrazolones is deep yellow, almost indistinguishable to the eye from those of the benzeneazopyrazolones, the azo-compounds derived from 1-β-anthraquinonyl-3-methyl-5-pyrazolone, notwithstanding the red colour of this compound, showing practically the same colour as those in which the anthraquinone nucleus is absent from the 1-position of the pyrazolone ring. This agrees well with Hewitt's theory (T., 1907, **91**, 1251), since the two carbonyl groups in the anthraquinone nucleus cut short the chain of double and single bonds, isolating the benzene ring beyond, so that it cannot add its effect, and thus the net result on the colour of an anthraquinone group in an azo-compound of this type is practically that of a single benzene ring.

Experimental.

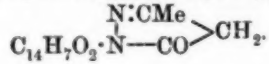
β-Anthraquinonylhydrazine.—For the purpose of this research, a considerable quantity of this hydrazine was required. The

synthesis has been described in detail by Möhlau, Viertel, and Reiner in a comprehensive paper (*Ber.*, 1912, **45**, 2233), and also by Möhlau (*ibid.*, p. 2244). The latter paper deals with the preparation from β-chloroanthraquinone by heating with hydrazine hydrate, but as the yields are only about 20 per cent., the process is useless on the large scale. The former paper is an account of the process outlined in D.R.-P. 163447, consisting in the reduction of β-anthraquinonediazonium sulphate in aqueous solution with potassium hydrogen sulphite, followed by hydrolysis of the hydrazinedisulphonic acid with hydrochloric acid. Owing to the fact that all the intermediate compounds have to be isolated in the solid state, the process is lengthy and cumbersome, on account of the rather large volume of water necessary for the sparingly soluble β-anthraquinonediazonium sulphate. The reduction of the diazonium chloride with stannous chloride has therefore been tried.

If β-aminoanthraquinone is boiled with excess of concentrated hydrochloric acid until completely converted to the hydrochloride, it can be diazotised at the ordinary temperature as readily as in concentrated sulphuric acid. Completion is shown when a drop of the liquid diluted with water gives yellow diazonium sulphate, soluble on shaking, instead of aminoanthraquinone in red flakes.

The action of stannous chloride on such a solution is complex and leads to poor yields of β-anthraquinonylhydrazine. Even when strongly cooled with ice and salt, nitrogen is evolved during the reaction, and the total nitrogen content of the final product never rises above 7·5 per cent. This seems to be due to a two-fold cause. First, the anthraquinone–carbonyl groups are more easily reduced than the diazo-group, and, secondly, steric hindrance causes the general sluggishness of the α-hydrogen in the hydrazine, reducing agents not being able to add this hydrogen, thus causing fission of the diazonium chloride to take place instead. It was further found that the addition of one molecule of stannic chloride caused the reaction to proceed more smoothly, a green, intermediate product being formed, but on isolating the free base it gave no better results on analysis. The hydrazone prepared from this hydrazine was purified only with difficulty, and, finally, the bulk of the hydrazine was prepared by the use of potassium salts, which give better yields and more uniform results than those of sodium, a constant yield of 70 per cent. being obtained.

1-β-Anthraquinonyl-3-methyl-5-pyrazolone,



$C_{14}H_7O_2 \cdot N(N{:}CMe)—CO > CH_2$.

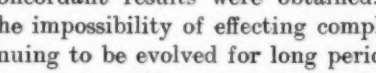
β-Anthraquinonylhydrazine was condensed with ethyl acetoacetate in amyl alcohol solution, and the hydrazone recrystallised from alcohol. Ten grams of this boiled with 100 c.c. of acetic anhydride gave 7·5 grams of the acetylpyrazolone, which was dissolved in a mixture of 200 c.c. of glacial acetic acid and 75 c.c. of hydrochloric acid, and hydrolysed by two hours' boiling, latterly with the addition of animal charcoal. The mixture was cooled, filtered, and poured into excess of water, when *1-β-anthraquinonyl-3-methyl-5-pyrazolone* separated as a yellowish-red, gelatinous mass, which was washed many times with cold water and dried at 100°. The yield was 6·5 grams.

The pyrazolone is soluble in glacial acetic acid to an orange solution, which deposits minute, red crystals on cooling, more readily so in pyridine, but only sparingly so in alcohol and most other organic solvents; insoluble in water, dilute acids, or alkalis, but giving a red solution in concentrated sulphuric acid and a port-wine coloured vat in alkaline hyposulphite.

It was recrystallised from pyridine, giving an orange powder, but although many combustions were carried out, neither satisfactory nor concordant results were obtained. This would seem to be due to the impossibility of effecting complete combustion, the nitrogen continuing to be evolved for long periods even at a bright red heat. The same trouble occurred to a less degree with the azo-derivatives, heating having to be continued for an unusual time before nitrogen ceased to be evolved.

The following reactions, characteristic of the pyrazolones, were shown. In acetic acid solution the compound readily reacts with nitrous acid to give a sparingly soluble, pale yellow iso*nitroso*-compound. Bromine water added to the same solution is at once decolorised, and a yellow precipitate of the dibromopyrazolone is formed. So far, a definite member of the antipyrine group has not been obtained.

4-Benzeneazo-1-β-anthraquinonyl-3-methyl-5-pyrazolone,

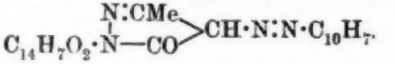


$C_{14}H_7O_2 \cdot N(N{:}CMe)—CO > CH{\cdot}N{:}NPh$.

To a solution of the pyrazolone in glacial acetic acid, the requisite quantity of benzenediazonium chloride was added. In the presence of sodium acetate, combination at once took place, a

yellow, gelatinous mass separating. After stirring for an hour at 0°, it was poured into water, collected, washed, and dried. It crystallises from pyridine, in which it is very readily soluble, in minute, yellow needles. It is soluble in nitrobenzene and, to a smaller extent, in glacial acetic acid; in concentrated sulphuric acid it gives a deep orange solution (Found: N = 13·58. $C_{24}H_{16}O_3N_4$ requires N = 13·71 per cent.).

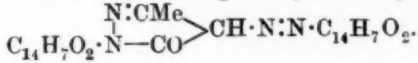
4-α-*Naphthaleneazo*-1-β-*anthraquinonyl*-3-*methyl*-5-*pyrazolone* and 4-β-*Naphthaleneazo*-1-β-*anthraquinonyl*-3-*methyl*-5-*pyrazolone*,



These were prepared in exactly the same way as the benzeneazo-compound. The former was obtained in minute, vermilion needles on crystallisation from pyridine, in which it is very sparingly soluble (about 0·75 gram in 100 c.c.). It gives a purple solution in concentrated sulphuric acid, whereas the β-naphthaleneazo-compound is deep orange in this solvent, the usual test which serves to distinguish the two isomerides, no matter what the 1-substituent of the pyrazolone ring is (Found: N = 12·06. $C_{28}H_{18}O_3N_4$ requires N = 12·22 per cent.).

The second compound, being almost insoluble in pyridine, was crystallised from nitrobenzene, giving a dull red powder. Both are insoluble in most organic solvents (Found: N = 12·10. $C_{28}H_{18}O_3N_4$ requires N = 12·22 per cent.).

4-β-*Anthraquinoneazo*-1-β-*anthraquinonyl*-3-*methyl*-5-*pyrazolone*,



β-Aminoanthraquinone (1·1 grams), after conversion to the hydrochloride, was diazotised in 30 c.c. of glacial acetic acid with 30 per cent. excess of amyl nitrite (Kaufler, *Zeitsch. Farben-Ind.*, 1903, **2**, 469). This was combined with 1·5 grams of the pyrazolone in acetic acid solution, giving a theoretical yield of the crude azo-compound. When crystallised from nitrobenzene, it forms fine, microscopic, yellow needles; variation of the conditions failed to produce any other form. It is insoluble in all solvents except nitrobenzene, and, to a less extent, in pyridine (Found: N = 10·26. $C_{32}H_{18}O_5N_4$ requires N = 10·39 per cent.).

4-β-Anthraquinoneazo-3-methyl-5-pyrazolone,

$$\begin{matrix} N{=}CMe \\ | \\ NH\cdot CO \end{matrix}\!\!>\!CH\cdot N{:}N\cdot C_{14}H_7O_2.$$

β-Aminoanthraquinone (2·5 grams) was dissolved in 19 c.c. of sulphuric acid (D 1·84) with mechanical stirring. The beaker was surrounded with a water-jacket, and 4·5 grams of dry, crushed ice were added to the solution. In five minutes, a voluminous, white paste of β-aminoanthraquinone sulphate was formed. A solution of 1 gram of sodium nitrite was then added from a tap funnel with a very fine nozzle, so that an hour elapsed before all had been run in, whilst the temperature of the acid and the surrounding bath was allowed to rise to 30° under the heat of dilution. As the diazotisation proceeded, the β-aminoanthraquinone sulphate dissolved, and, on completion, a clear, brown solution resulted, a drop of which, added to water, gave a yellow precipitate, dissolving to a very pale yellow solution on shaking. Sufficient ice to dilute the warm solution enough to start the crystallisation of the β-anthraquinonediazonium sulphate was added, and the whole set aside to cool. In half an hour the diazonium salt crystallised in shining, yellow plates, the contents of the beaker setting solid. The mass was scraped out on to crushed ice, collected, and washed once with ice-water. The β-anthraquinonediazonium sulphate was obtained in this way as a yellow, stable, crystalline powder in a yield of 87 per cent. of the theoretical. It was dissolved by stirring into 400 c.c. of water at 20° and decomposed with a solution of 5 grams of sodium acetate.

Ten grams of 3-methyl-5-pyrazolone having been dissolved in 250 c.c. of water, the diazo-solution was added with stirring, and immediately the azo-compound separated in yellow flakes. It was collected, washed twice with hot water, and dried at 100°; the yield was theoretical.

This compound was found to be characterised by extreme insolubility in all organic solvents. It was crystallised from pyridine, in which it dissolved to the extent of less than 1 per cent., the crystals forming microscopic needles. It was also sparingly soluble in nitrobenzene or amyl alcohol; in concentrated sulphuric acid, the solution was orange (Found: N = 17·12. $C_{12}H_{12}O_3N_4$ requires N = 16·90 per cent.).

When warmed with dilute sodium hydroxide solution, it dissolved readily, giving a deep purple solution. On salting the hot solution, shining, purplish-black crystals were deposited, and on acidifying a solution of these, the original azopyrazolone was precipitated as a yellow jelly. By titration of a solution with 0·1*N*-

hydrochloric acid, using the above colour change as indicator, it was found that the salt contained one atom of sodium.

4-β-Anthraquinoneazo-1-β-naphthyl-3-methyl-5-pyrazolone,

$$C_{10}H_7\cdot N\begin{<}CO \\ N{:}CMe\end{>}CH\cdot N{:}N\cdot C_{14}H_7O_2.$$

Four grams of 1-β-naphthyl-3-methyl-5-pyrazolone dissolved in glacial acetic acid were combined with the anthraquinonediazonium sulphate, prepared from 4·6 grams of β-aminoanthraquinone diazotised as above. The azo-compound, obtained as a flocculent, orange mass on dilution with water, was collected, washed twice with cold water and once with hot, and dried at 100°. It gave brick-red needles when crystallised from nitrobenzene, in which it is fairly soluble at the boiling point. Crystallisation of the cool solution diluted with alcohol, conditions under which 4-β-anthraquinoneazo-1-phenyl-3-methyl-5-pyrazolone gives a large proportion of the yellow form, failed to give any other variety. It is also soluble in pyridine or glacial acetic acid, whilst in alcoholic sodium hydroxide it gives the typical purple solution; in concentrated sulphuric acid its solution is deep red (Found: N = 12·46. $C_{28}H_{18}O_3N_4$ requires N = 12·25 per cent.).

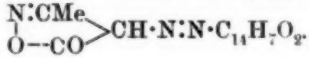
Attempts were made to prepare the isomeric 4-β-anthraquinoneazo-1-α-naphthyl-3-methyl-5-pyrazolone, but the results were unsatisfactory, and a pure substance was not obtained.

Ethyl β-Anthraquinoneazoacetoacetate,

$$C_{14}H_7O_2\cdot N{:}N\cdot CHAc\cdot CO_2Et.$$

The β-anthraquinonediazonium sulphate resulting from the diazotisation of 10 grams of β-aminoanthraquinone was dissolved in a litre of water to which were added 20 grams of sodium acetate. To this, a solution of 5·1 grams of ethyl acetoacetate dissolved in 39 c.c. of *N*-sodium hydroxide was added, and the whole stirred until the odour of the ester had disappeared. The yellow azo-compound, being quite insoluble in water, separated at once, and was collected, washed, and dried. The yield was theoretical, calculating from the anthraquinonediazonium sulphate used. The crude substance had a green tinge, but, after boiling with animal charcoal and recrystallising from glacial acetic acid, it gave a yellow powder melting at 216—218°. It is surprisingly soluble for an anthraquinone derivative, dissolving in alcohol, chloroform, benzene, toluene, nitrobenzene, or pyridine. Alkali hydroxide turns it purple, but it is sparingly soluble, and acids precipitate it as a yellow jelly (Found: N = 7·84. $C_{20}H_{16}O_5N_2$ requires N = 7·69 per cent.).

*4-β-Anthraquinoneazo-3-methyl*isooxazolone,



Eight grams of ethyl β-anthraquinoneazoacetoacetate were dissolved in a mixture of 175 c.c. of glacial acetic acid and 25 c.c. of an aqueous solution of 3 grams of sodium acetate. To the warm solution, 1·5 grams of hydroxylamine hydrochloride, dissolved in 10 c.c. of water, were added, and the whole was boiled for two hours, when a drop no longer showed a reducing action on Fehling's solution. The colour was then orange. Animal charcoal was added, and the whole boiled for a further ten minutes, filtered hot through asbestos, and slowly cooled. A mass of orange, needle-shaped crystals was deposited, and these were collected and dried; the yield was 6 grams. The substance melted and decomposed at 188—191°. It was soluble in acetic acid, alcohol, chloroform, benzene, or toluene, insoluble in water or dilute mineral acids, and sparingly soluble to a purple solution in alkali hydroxide (Found: N = 12·01. $C_{19}H_{18}O_4N_3$ requires N = 12·68 per cent.).

On treating an acetic acid solution of the *iso*oxazolone with hydrazine, so voluminous a precipitate of 4-β-anthraquinoneazo-3-methyl-5-pyrazolone was obtained that the whole set solid. This substance was identified by the properties given above. With phenylhydrazine, a small crop of 4-β-anthraquinoneazo-1-phenyl-3-methyl-5-pyrazolone was obtained and identified by its melting point. With the naphthylhydrazines, the products were too impure and tarry to identify with certainty. When 1 gram was boiled with 0·9 gram of β-anthraquinonylhydrazine, a precipitate of 0·8 gram of a red substance was obtained. By its insolubility in all solvents, except nitrobenzene, and its giving a reddish-purple solution in alkaline hyposulphite, it was concluded that it was 4-β-anthraquinoneazo-1-β-anthraquinonyl-3-methyl-5-pyrazolone, but the yield being so poor and the product so impure, this method of preparation was abandoned, as being too wasteful of the valuable β-anthraquinonylhydrazine.

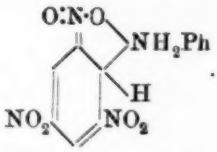
The author wishes to express his thanks to the Salters' Institute of Industrial Chemistry for a Fellowship which enabled the work to be conducted, to Sir William Pope for his inspiration and interest, and to Dr. M. O. Forster for his guidance throughout the course of the work.

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, September 18th,* 1920.]

CXXXVII.—*The Action of Amines on Trinitrophenylmethylnitroamine.*

By Thomas Campbell James, James Ivor Morgan Jones, and Robert Illtyd Lewis.

It is a well-known property of polynitro-aromatic compounds that they form additive derivatives with various types of aromatic substances, such as hydrocarbons, phenols, amines, etc. The most recent work on these derivatives has been carried out by Sudborough and his collaborators, who have examined in detail the formation and properties of a large series of the additive compounds formed by *s*-trinitrobenzene. In a review of the compounds prepared by them, Sudborough and Beard (T., 1910, **97**, 773) were led to suggest a possible formula for the compound of trinitrobenzene with aniline, representing it as possessing a hemi-quinonoid structure:



The present investigation was undertaken with a view to ascertain whether trinitrophenylmethylnitroamine (tetryl) forms additive compounds of a similar type to *s*-trinitrobenzene. It was observed that solutions of this substance in a variety of solvents became deeply coloured on the addition of any amine, primary, secondary, or tertiary, except in such cases where the amine contains strongly negative radicles, and in a large number of cases it has been possible to isolate from these solutions definite crystalline compounds, which are, without exception, compounds of tetryl and the base, united in equimolecular proportions. Owing to the fact that the additive compounds are largely dissociated in solution, the separation of the pure product is difficult in cases where the constituents are less readily soluble than the additive product.

The general conclusions drawn by Sudborough and Beard (*loc. cit.*) regarding stability and depth of colour have been confirmed, although the stability of this series of compounds is, on the whole, less than that of the corresponding compounds of the trinitrobenzene series. Thus, additive compounds of tetryl with phenols and tertiary amines have not been isolated in a pure state, although evidence of their formation is afforded by the production of a red colour when solutions of the components are mixed, and also, in

some cases, by an investigation of the melting points of mixtures of the components. Hydrocarbons and nitrophenols do not yield additive products.

The chief point of difference between the additive compounds under consideration and those of the trinitrobenzene series is that, in many cases, like the additive compounds of picryl chloride with bases, described by Sudborough and Picton (T., 1906, **89**, 583), they readily undergo a change to a condensed compound; thus, the compound of trinitrophenylmethylnitroamine and aniline, on storing in a sealed tube or on slow crystallisation from a hot solvent, yields 2:4:6-trinitrodiphenylamine, condensation apparently occurring according to the equation

$$C_6H_2(NO_2)_3\cdot NMe\cdot NO_2,NH_2Ph = C_6H_2(NO_2)_3\cdot NHPh + NHMe\cdot NO_2.$$

We have not succeeded in isolating the methylnitroamine, despite various attempts, and it is probably decomposed during the condensation. The products are identical with those formed by the action of picryl chloride on the amine, and in a number of cases exist in two or more modifications differing in crystalline form and colour (compare Sudborough and Picton, *loc. cit.*; Busch and Pungs, *J. pr. Chem.*, 1909, [ii], **79**, 546; Hantzsch, *Ber.*, 1910, **43**, 1678). It is of interest to note, however, that the first product is generally of a red colour, whilst yellow or orange modifications are obtained by the use of picryl chloride, this being due to the presence of hydrogen chloride, which is instrumental in converting red forms into yellow.

Molecular-weight determinations of the additive compounds indicate that, notwithstanding the development of deep colour in the solutions, dissociation into the components is almost complete in dilute solution.

Experimental.

The method of work consisted, in general, in allowing a cold saturated solution of tetryl in alcohol, acetone, or benzene, and treated with rather more than one molecular proportion of the amine in the same solvent or in ether, to remain until crystallisation took place. In many cases, crystals of the additive compound were deposited with ease; in others, condensation took place, and the picryl derivative was obtained as first product. When the mixed solutions were heated for some time on a water-bath or when the crystallisation was prolonged by leaving the solvent to evaporate slowly on a hot plate, the condensation compound was usually deposited.

Ammonia.—The addition of an alcoholic solution of ammonia (one and two equivalents, respectively, were used in different

experiments) to a saturated alcoholic solution of tetryl yielded a deep red solution of an additive compound, which it was not possible to isolate. The deep colour gradually disappeared on warming, and from the resulting yellow solution, picramide (m. p. 188°), in a yield corresponding with 53 per cent. of the theoretical, crystallised out. The filtrate, on evaporation, provided a further yield of crystals, which proved to be ammonium picrate.

When dry ammonia was passed into a solution of tetryl in benzene, little action took place, but on the addition of a small amount of acetone, a deep red solution was produced, from which a fluorescent, green oil separated. This solidified, on keeping, to a deep green mass, which, when freshly prepared, had a strong odour of ammonia. It is soluble in water or alcohol, giving orange-coloured solutions, but it has not been obtained in good crystalline form, and the melting point is indefinite, the substance decomposing explosively on heating above 100°. After excess of ammonia is removed, the substance contains C = 34·19, H = 3·61, and N = 24·97 per cent., corresponding with the formula $C_{10}H_{12}O_8N_6$.

Methylamine.—When treated with an alcoholic solution of methylamine, tetryl gives a deep red-coloured solution, which, after slight warming, deposits reddish-brown needles (m. p. 112°) consisting of 2:4:6-trinitromethylaniline (Romburgh, *Rec. trav. chim.*, 1883, **2**, 105). On recrystallising from alcohol containing a small proportion of acid, pure, yellow needles melting at 114·8° are obtained (Found: N = 23·45. Calc.: N = 23·09 per cent.).

Benzylamine.—This yields 2 : 4 : 6-*trinitrophenylbenzylamine*, consisting of chocolate-coloured needles (m. p. 143·3°), which, when crystallised from alcohol containing a little acid, becomes golden-yellow and melts at 144·8° (Found: N = 17·70 $C_{13}H_{10}O_6N_4$ requires N = 17·61 per cent.).

Aniline.—The additive *compound* of tetryl with aniline was readily obtained from benzene solution, and forms orange-red plates melting at 64° (Found: N = 21·35. $C_{13}H_{12}O_8N_6$ requires N = 22·11 per cent.).

The substance decomposes on keeping in the air, by treatment with acids, and by treatment with many solvents, regenerating tetryl (0·5425 treated with acid gave 0·4064 tetryl, = 74·91. Calc.: tetryl = 75·48 per cent.).

On keeping in a sealed tube for several weeks, the substance became moist, and the product on crystallisation proved to be 2:4:6-trinitrodiphenylamine. This substance is also obtained by slow crystallisation of the original mixture from warm benzene, acetone, or alcohol solutions. It forms orange crystals melting at

178°, corresponding with the description of Bamberger and Müller (*Ber.*, 1900, **33**, 188).

o-*Toluidine*.—An additive *compound* with tetryl is readily obtained by adding a slight excess of the base to a hot solution of tetryl in benzene solution, and allowing to crystallise. It consists of brick-red crystals melting at 63° (Found: N = 21·18; tetryl = 72·7. $C_{14}H_{14}O_8N_6$ requires N = 21·32; tetryl = 72·8 per cent.).

The substance decomposes on exposure to the atmosphere and also on recrystallisation, yielding tetryl. It does not, however, yield a condensation product, and 2:4:6-trinitrophenyl-*o*-tolylamine is not formed, even when the mixture of components is boiled for forty-eight hours in a reflux apparatus using various solvents.

m-*Toluidine*.—The additive compound in this case has not been obtained in a pure form, as it is rapidly changed, even at the ordinary temperature, to a condensed derivative. The product obtained from a mixture of the components in benzene solution consists of deep red needles melting at about 80°, which on treatment with acid regenerate tetryl. On warming this product with benzene or with a mixture of chloroform and light petroleum and allowing to crystallise, bright scarlet needles are deposited which melt at 118·5° (Found: N = 17·37. $C_{13}H_{10}O_6N_4$ requires N = 17·73 per cent.).

This substance, when first prepared, could be recrystallised from alcohol without change, but on the addition of a drop of acid to a saturated solution in alcohol, orange-yellow, prismatic crystals separated. These melt at 129° and correspond with 2:4:6-trinitrophenyl-*m*-tolylamine, as described by Busch and Pungs (*J. pr. Chem.*, 1909, [ii], **79**, 550). These authors state that the substance occurs in two forms, an orange modification (m. p. 129·5°) and a pure yellow form (m. p. 130°). The forms obtained by us are readily soluble in alkali hydroxide, yielding deep red solutions, which, on acidifying, yield a pure yellow form melting at 129°. We have been unable, so far, to reconvert the stable yellow form into the labile scarlet form melting at 118·5°.

p-*Toluidine*.—In the case of this amine, an additive *compound* with trinitrophenylmethylnitroamine is readily obtained by crystallising a mixture of the components from benzene or alcohol. It consists of deep red needles melting at 54°, which are readily decomposed by acids, regenerating tetryl (Found: N = 20·82; tetryl = 72·1. $C_{14}H_{14}O_8N_6$ requires N = 21·32; tetryl = 72·8 per cent.).

The condensation compound, 2:4:6-trinitrophenyl-*p*-tolylamine, was obtained in the manner described above, and was isolated in

the two forms described by Busch and Pungs (*loc. cit.*, p. 543) as orange-yellow needles (m. p. 163—164°) and blood-red prisms (m. p. 165°).

m-Xylidine.—This base yields with tetryl a very unstable additive compound, which undergoes condensation very readily to form 2:4:6-*trinitrophenyl*-m-*xylylamine*,

$$C_6H_2(NO_2)_3\cdot NH\cdot C_6H_3Me_2;$$

this crystallises in orange-yellow needles melting at 157° (Found: N=17·11. $C_{14}H_{12}O_6N_4$ requires N=16·86 per cent.).

o-Anisidine.—We were unable to isolate an additive compound in this case, although the colour of the solution indicated that such a compound is formed. From a warm solution in alcohol, red crystals of 2′:4′:6′-trinitro-2-methoxydiphenylamine separated, melting at 143° (Busch and Pungs, *loc. cit.*, p. 552, give 142°).

p-Anisidine.—In this case, again, no additive compound was isolated, for 2′:4′:6′-trinitro-4-methoxydiphenylamine was obtained even when cold solutions of the components were mixed. This consists of orange-red needles melting at 172·5° (Found: N=16·75. Calc.: N=16·77 per cent.).

Busch and Pungs (*loc. cit.*, p. 552) describe this compound as melting at 138°. We have repeated their preparation of the substance from picryl chloride and *p*-anisidine, and find that the product melts at 172·5°, as given above.

p-Aminophenol.—The additive compound in this case has not been obtained pure, and readily passes into the condensed derivative, 2′:4′:6′-trinitro-4-hydroxydiphenylamine, which consists of brick-red needles melting at 174° (Turpin, T., 1891, **59**, 718).

α-Naphthylamine.—The additive *compound* of this base is readily obtained by crystallising a mixture of the components in equivalent amounts from benzene. It consists of well-defined black prisms melting at 94°. The compound is of considerably greater stability than the additive compounds previously described, but is partly decomposed by crystallisation from many solvents, and completely by warming with acids (Found: N=19·73; tetryl=66·46. $C_{17}H_{14}O_8N_6$ requires N=19·53; tetryl=66·73 per cent.).

No condensation product is formed, even after prolonged boiling of the additive compound or of a mixture of the components in a variety of solvents.

β-Naphthylamine.—The additive *compound* is similar to the above, and is obtained in black prisms melting at 90° (Found: N=19·72. $C_{17}H_{14}O_8N_6$ requires N=19·53 per cent.).

The compound is fairly stable and does not yield a condensed derivative.

m-*Phenylenediamine*.—The additive *compound* of this base is readily obtained by crystallisation from benzene solution, and consists of silky, brown needles melting at 84°, which are moderately stable, but are partly decomposed by recrystallisation and completely by warming with acids (Found: N = 24·94. $C_{13}H_{13}O_8N_7$ requires N = 24·81 per cent.).

The condensation compound, 2:4:6-trinitro-*m*-aminodiphenylamine, is obtained by slow crystallisation from hot acetone, and forms a deep red, crystalline powder melting at 207° (compare Jaubert, *Ber.*, 1898, **31**, 1182).

Methylaniline.—This base yields an additive *compound* with trinitrophenylmethylnitroamine, which consists of deep red plates melting at 86° (Found: N = 21·86. $C_{14}H_{14}O_8N_6$ requires N = 21·32 per cent.).

The condensation compound has not been obtained by our general method.

Dimethylaniline, ethylaniline, and diethylaniline all yield deeply coloured solutions when mixed with solutions of tetryl, but pure additive compounds have not yet been obtained in these cases. Moreover, condensation to picryl derivatives does not occur even after prolonged boiling in alcohol or acetone solutions.

Similarly, *m*-nitroaniline and *p*-nitroaniline yield slightly coloured solutions with tetryl, but the separation of pure additive compounds has not been achieved. An investigation of the freezing-point curves of mixtures of these bases with tetryl indicates that unstable molecular compounds can exist.

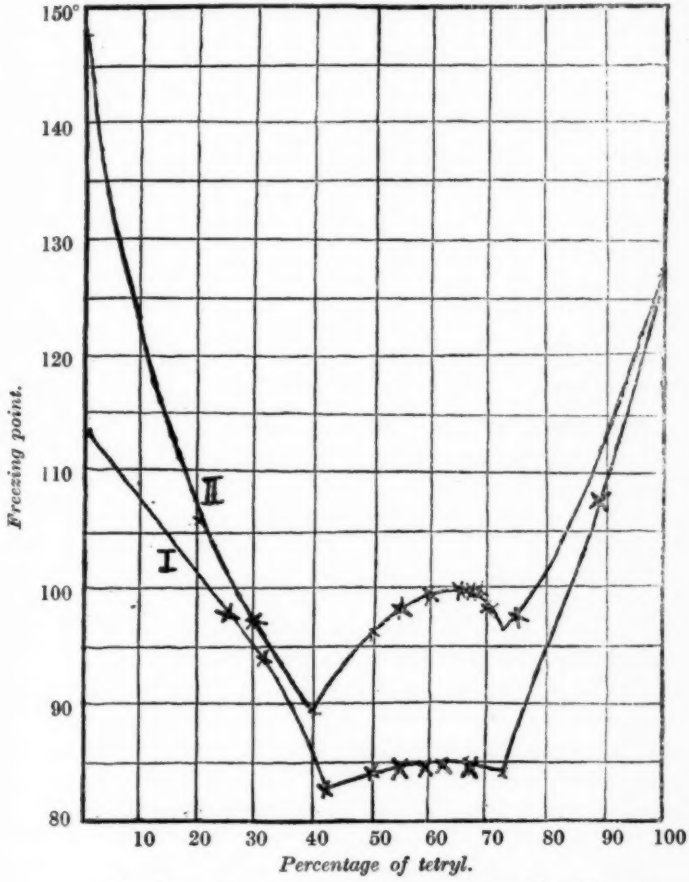
Halogen-substituted amines give only feeble colorations with solutions of tetryl, and form no additive compounds; condensation is also not possible.

Summary and Conclusion.

Trinitrophenylmethylnitroamine (tetryl) readily forms equimolecular additive compounds with the simpler amines, which in many cases readily condense to form picrylamines. The presence of alkyl substituents in the ortho-position in the amine does not affect the formation of the additive compound, but inhibits the condensation. The presence of the methoxy-group in the ortho-position does not, however, prevent the condensation (compare *o*-toluidine and *o*-anisidine). On the other hand, substitution in the meta-position renders the molecular compound unstable, and it readily passes into the corresponding picrylamine. The naphthylamines and the secondary amines yield stable additive

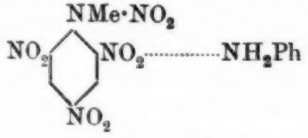
compounds, which do not pass into condensation derivatives (compare Sudborough and Picton, *loc. cit.*, p. 589).

According to Werner, the components of molecular compounds

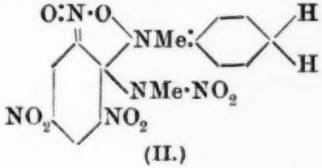


Freezing-point curves of tetryl–*m*-nitroaniline (I) and tetryl–*p*-nitroaniline mixtures (II).

of this type are to be represented as united by the residual or auxiliary valencies of the nitro- and amino-groups (I):



(I.)



(II.)

It may be pointed out, however, that a representation in accordance with Sudborough and Beard's suggestion (p. 1273) brings the nitroamine group into close proximity with the amino-group. If the amine be represented as possessing a hemi-quinonoid structure, the intense colour of the molecular compounds and the comparative stability of the derivatives of secondary amines may also be explained. Thus the molecular compound with methylaniline might be represented as (II).

The influence of substituents in the phenyl group of the amine on the ease with which condensation can take place is not obvious in a formula of this type, whereas in the case of the Werner formula such substituents may be represented as modifying the amount of residual valency, whereby the amine is attached to the nitro-group.

We desire to thank Mr. Talfryn James for assistance in the preparation of some of the substances described.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
ABERYSTWYTH. [*Received, September* 13*th*, 1920.]

CXXXVIII.—*The Influence of Hydrogen Sulphide on the Occlusion of Hydrogen by Palladium. Part II.*

By EDWARD BRADFORD MAXTED.

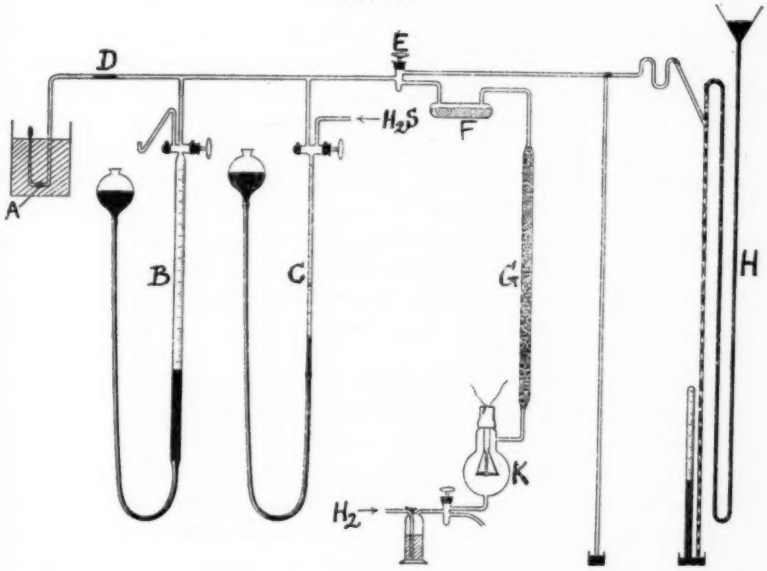
IN a previous paper (T., 1919, **115**, 1050) it has been shown that whilst comparatively small quantities of occluded hydrogen sulphide are sufficient totally to inhibit the subsequent occlusion of hydrogen by palladium, this occluded hydrogen sulphide, on being heated to 100° in a vacuum, evolves an equal volume of hydrogen and passes into a sulphur complex which is far less poisonous than hydrogen sulphide itself. The inhibitive effect of sulphur in the latter form could be predicted by assuming the formation of a complex Pd_4S, which is incapable of occlusion, and ascribing to the residual palladium its normal occlusive power for hydrogen.

In the previous paper, the minimum volume of hydrogen sulphide, as such, required for the complete inhibition of the occlusive power of palladium for hydrogen, was not determined, it being noted, however, that the volume of gas absorbed by palladium on exposure for a short time to hydrogen sulphide—this amounting in an experiment to 13·5 c.c. per gram of metal—

was sufficient to prevent the ordinary occlusion of hydrogen on subsequently admitting the gas.

The subject has now been investigated further, with the object of following quantitatively the inhibitive effect of successive increments in the hydrogen sulphide content of a given weight of palladium, this hydrogen sulphide being present in the form in which it is originally occluded and being added to the palladium in small known quantities, which for the majority of the measurements were less than the volume required for saturation. The poisoning curve for undecomposed occluded hydrogen sulphide was

FIG. 1.



found to be linear in form. Evidence was also obtained of the gradual and spontaneous dissociation of the occluded hydrogen sulphide even at the ordinary temperature, with the formation of hydrogen and of the Pd_4S complex. This reaction is accompanied by a corresponding change in the occlusive power.

EXPERIMENTAL.

The apparatus employed is shown diagrammatically in Fig. 1. It consists of a small absorption tube, *A*, containing a known weight of palladium, which was weighed out as chloride and reduced in situ, as before. In order to introduce into the system hydrogen

or hydrogen sulphide, as required, two gas burettes, *B* and *C*, were provided. These had a capacity of 25 c.c. and 5 c.c. respectively, the larger burette being employed for hydrogen. The system could be exhausted by means of a Sprengel pump, *H*, or, where more convenient, by lowering and raising the mercury in *B*, the three-way cock being turned as required. All parts of the apparatus were joined by fusion, and all stopcocks were mercury-sealed. In view of the inhibitive effect of mercury on the occlusive power of palladium observed by Paal and Hartmann (*Ber.*, 1918, **51**, 711), a short plug of gold leaf, *D*, was inserted as a precaution against the possible penetration of traces of mercury vapour into the absorption tube. The hydrogen used for reducing the palladium chloride in *A* and for filling *B* was obtained from a cylinder of the electrolytic gas, and was freed from traces of oxygen by passage through a "half-watt" lamp, *K*, followed by a soda-lime tube, *G*, and phosphoric oxide tube, *F*. The hydrogen sulphide was prepared by the action of heat on magnesium hydrosulphide, and was dried by passage over calcium chloride. In order to reduce the volume of the absorbing system to as small a value as possible, capillary connexions were employed throughout. The volume of this system was redetermined for each absorption tube, the value being required in order to obtain the true occlusive power of the preparation from the volume of hydrogen absorbed from *B*.

Each measurement was begun by sealing on a fresh absorption tube containing a known weight of palladium chloride. This was reduced to metal by means of hydrogen at 100°, the current of gas passing out of the system by way of the open end of *A*, which was subsequently sealed off. The volume of hydrogen which was capable of being evolved at 100° or occluded at the ordinary temperature having been determined, as before, *A* was exhausted at 100°, and, after cooling to the ordinary temperature, *E* was closed and a known small volume of hydrogen sulphide allowed to pass from *C* into the absorption tube. This gas was found to be quickly and practically completely absorbed by the palladium, and, on subsequently admitting hydrogen from *B*, occlusion of this gas took place to an extent dependent on the degree of poisoning which had been induced by the preliminary treatment with hydrogen sulphide.

The results of the various measurements are summarised in table I, in which the experiments are arranged in order of increasing hydrogen sulphide content. The volumes of gas are in every case reduced to 0° and 760 mm., the experiments being, however, carried out at 20°.

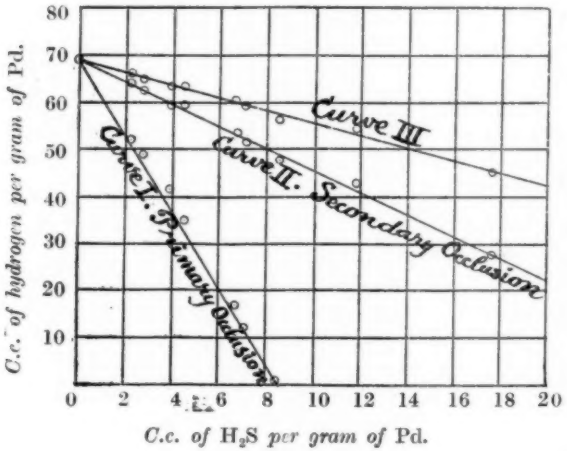
TABLE I.

No. of expt.	Weight of palladium. Gram.	Original occlusive power. C.c. H_2.	Equivalent occlusive power in c.c. H_2 per gram Pd.	C.c. H_2S. absorbed.	C.c. H_2S per gram Pd.	Subsequent primary occlusion. C.c. H_2.	Equivalent occlusive power in c.c. H_2 per gram Pd.	Total occlusion. C.c. H_2.	Total occlusive power per gram Pd.
1	0·1033	7·25	70·0	0·23	2·2	6·1	52·0	6·6	64·0
2	0·2380	16·45	69·2	0·65	2·74	11·7	49·0	14·85	62·5
3	0·0976	6·85	70·1	0·38	3·9	4·1	41·7	5·8	59·5
4	0·1714	12·1	70·5	0·78	4·56	6·0	35·0	10·25	59·8
5	0·2000	14·1	70·5	1·35	6·75	3·4	17·0	10·75	53·7
6	0·2795	19·0	68·0	2·00	7·16	3·5	12·5	14·25	51·9
7	0·1890	13·1	69·3	1·61	8·52	0·2	1·1	9·05	47·8
8	0·1422	9·9	69·6	1·68	11·8	Nil	Nil.	6·1	43·0
9	0·0993	6·75	68·0	1·75	17·6	Nil	Nil.	2·75	27·7

It will be seen that the occlusive power of palladium for hydrogen is diminished progressively by the presence of increasing concentrations of hydrogen sulphide. Provided that the ratio of hydrogen sulphide to palladium is less than a certain critical quantity, a volume of hydrogen, varying with the concentration of the inhibitant, is occluded at once in a normal manner, as is the case with unpoisoned palladium. This primary process of practically instantaneous absorption is followed by a secondary process, during which a further quantity of hydrogen is gradually and slowly occluded. Evidence will be adduced later in the present paper that secondary absorption is due to dissociation of the occluded hydrogen sulphide.

On passing through a critical value of about 8·5 c.c. of hydrogen

FIG. 2.

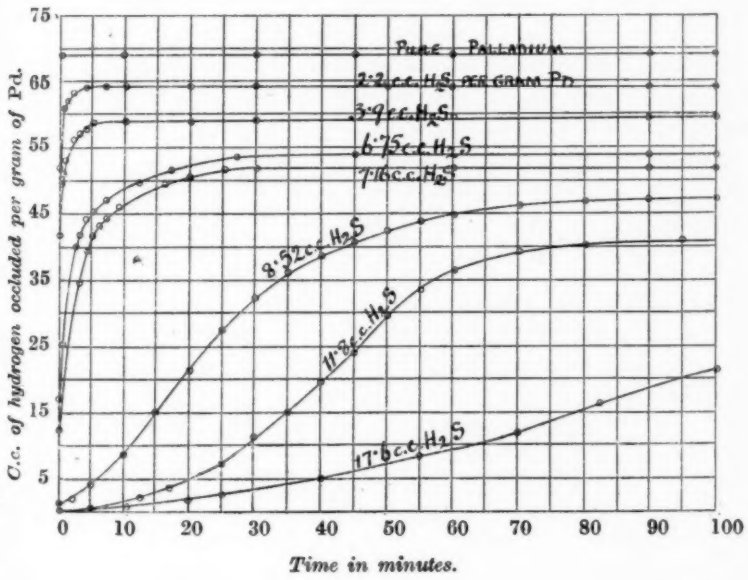


sulphide per gram of palladium, primary absorption ceases, and secondary occlusion only is observed; further, on plotting occlusive power against hydrogen sulphide content, it is seen that the influence of this inhibitant, both on primary occlusion and on total occlusion, is linear in nature. This result, which is analogous to that obtained for decomposed hydrogen sulphide, is illustrated in Curves I and II in Fig. 2.

In cases where the concentration of hydrogen sulphide is considerably in excess of that necessary totally to inhibit primary occlusion, the first stages of secondary absorption may take place sufficiently slowly to mask the process unless the system is kept under observation for a considerable time after admission of hydrogen. The process of secondary absorption, after beginning

slowly, gradually increases in velocity, and finally the velocity diminishes to zero as the limit of total occlusion is approached. With concentrations of hydrogen sulphide below the critical ratio, secondary absorption may, on the other hand, take place at a velocity sufficient to render necessary a very careful following of the movement of the mercury in the hydrogen burette, in order to map accurately the progress of the first stages of the process and to differentiate it from primary absorption. Measurements, in which readings of the volume occluded were taken, in such cases, every few seconds during the first stages of secondary occlusion,

FIG. 3.



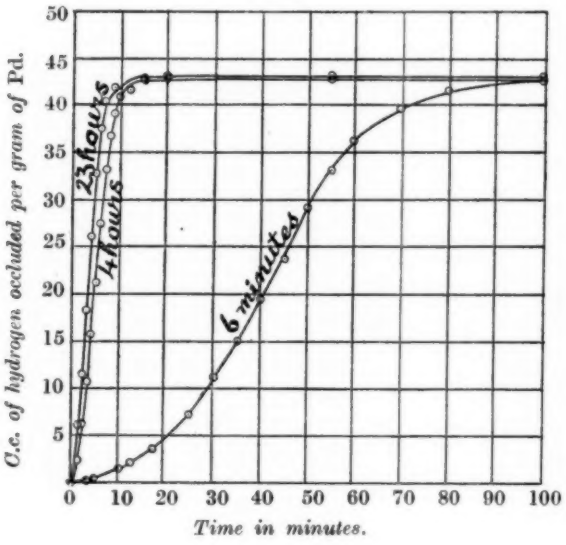
have, however, shown that the general form of this absorption curve, although more rapid, is similar to that observed with higher concentrations of hydrogen sulphide, in which secondary occlusion is slower and more easily followed. The form of the various absorption curves is well shown in Fig. 3, in which the progress of absorption of certain of the measurements is plotted against the time.

In order to obtain information respecting the nature of the process involved during secondary occlusion, careful analyses were made of the gas remaining in the absorption pipette after secondary absorption had taken place, for the purpose of ascertaining whether

or not hydrogen sulphide is evolved during the change, simultaneously with the slow absorption of hydrogen. In no case was hydrogen sulphide in appreciable quantity observed, and exhaustion of the gas, followed by the introduction of fresh hydrogen, also failed to cause the fresh increase in occlusive power which would be expected if secondary occlusion were due either to the gradual displacement of hydrogen sulphide by hydrogen or to the reduction of a sulphide complex, with evolution of the sulphur as hydrogen sulphide.

The process appears, on the other hand, to be due to a change

FIG. 4.



in the condition of the occluded hydrogen sulphide itself, in that the change in occlusive power is found to take place spontaneously on standing.

In order to investigate this point, three measurements were carried out with three specimens of palladium, which were in each case allowed to absorb about 11·8 c.c. of hydrogen sulphide per gram of palladium, the subsequent admission of hydrogen for the determination of the occlusive power being delayed for six minutes, four hours, and twenty-three hours respectively. The absorption curves obtained are reproduced in Fig. 4, from which it will be seen that whilst the final volume of hydrogen occluded by preparations containing an approximately equal volume of hydrogen sulphide is the same in each case, the form of the absorption curve

has been influenced by the time which has been allowed to elapse between treatment with hydrogen sulphide and subsequent measurement of the occlusive power for hydrogen, almost complete suppression of the slow process of secondary occlusion having been induced by allowing the system to stand.

The nature of the change undergone by occluded hydrogen sulphide during the comparatively slow passage of the system at 20° from a state of lower to one of higher occlusive power would seem to be similar to that obtained instantaneously at 100°, in which the hydrogen of the hydrogen sulphide has been shown to be evolved as such, the sulphur being retained by the palladium as a Pd_4S complex.

This view is supported by considering the dissociation reaction

$$H_2S \rightleftharpoons 2H + S$$

in connexion with the volume of hydrogen occluded during primary and secondary absorption. During this dissociation, a volume of hydrogen equal, whilst in the molecular condition, to that of the hydrogen sulphide occluded is set free and must be added to the volume of hydrogen subsequently absorbed in order to derive the true occlusive power of the preparation. The total volume of hydrogen thus contained in the palladium should, if the reaction postulated is the correct one, fall on the known poisoning curve, calculated on the basis of the presence of Pd_4S complex in amount equal to the sulphur contained in the hydrogen sulphide occluded.

The close agreement between the observed occlusive powers and the values calculated from the Pd_4S curve is shown in table II, the results being also plotted graphically in curve 3 of Fig. 2.

Table II.

No. of expt.	C.c. H_2S per gram palladium.	Hydrogen occluded. C.c.	Total hydrogen. C.c.	Total hydrogen calculated from Pd_4S curve.
1	2·2	64·0	66·2	66·0
2	2·74	62·5	65·2	65·4
3	3·9	59·5	63·4	63·8
4	4·56	59·8	64·4	62·9
5	6·75	53·7	60·5	60·0
6	7·16	51·9	59·1	59·5
7	8·52	47·8	56·3	57·7
8	11·8	43·0	54·8	53·3
9	17·6	27·7	45·3	45·6

For the purpose of the calculation required for the above table, the occlusive power for hydrogen of 1 gram of unpoisoned palladium, under the given conditions, has been taken as 69 c.c., this value being in agreement both with the measurements

contained in the present paper and with those previously published.

The palladium, in addition to functioning as an occluding medium, would thus appear to induce the catalytic dissociation of the occluding hydrogen sulphide. This gradual dissociation affords also a ready explanation of the non-existence of a definite solubility of hydrogen sulphide in palladium. It has previously been shown that, after preliminary saturation, a slow but continuous absorption of hydrogen sulphide takes place, occlusion of as much as 42 c.c. per gram being observed by allowing palladium to remain for three weeks in excess of hydrogen sulphide. It will be seen that the gradual disappearance of occluded hydrogen sulphide, as such, due to the passage of the sulphur into the Pd_4S form, should cause the system to cease to be saturated for hydrogen sulphide. Fresh hydrogen sulphide is thus occluded, and the process continues until the occluding palladium has been eliminated as Pd_4S complex. It would be expected that the catalytic activity of the palladium, necessary for causing dissociation, would also decrease progressively as poisoning proceeds, so that the velocity of this dissociation, and consequently of the absorption of fresh hydrogen sulphide, should rapidly diminish with increase in the sulphur content of the palladium. This decrease in the velocity of the dissociation of hydrogen sulphide with increasing sulphur content is demonstrated in a striking manner by the curves of Fig. 3.

It should be emphasised that the complex Pd_4S cannot, without further investigation, be assumed to be a true sulphide of palladium, the character of this complex having yet to be determined.

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CXXXIX.—*Catalysis in the Hydrolysis of Esters by Infra-red Radiation.*

By ERIC KEIGHTLEY RIDEAL and JAMES ARTHUR HAWKINS.

ACCORDING to the quantum radiation hypothesis of chemical and physical actions as developed by Trautz, Lewis, and Perrin (compare *Ann. Physique*, 1919, [ix], **11**, 5), molecules only become reactive after absorption of a definite amount of energy, the critical energy increment, although it appears probable that for

different reactions the degree of activation necessary may differ, yet these various stages of activation, corresponding with various critical energy increments, are related to one another in a simple manner. This energy acquired by the molecule is potential, and is assumed to be supplied by radiation; thus all reactions, in the broad sense of the term, are photochemical or photophysical. The chemical and physical effects produced by α-particles and electrons may be included, since the characteristics of photochemical reactions may be quantitatively interpreted with the greatest facility on a corpuscular theory of radiation.

Up to the present time, with the exception of the photochemical reactions taking place in the actinic part of the spectrum, there has been no direct proof of the validity of the extension of this hypothesis into the other parts of the spectrum, especially the infra-red, the arguments in favour of such an hypothesis being indirect, based on experimental data, such as the temperature-coefficient of chemical and physical reactions, the heats of formation of chemical compounds, or the latent heat of evaporation of the elements.

The temperature-coefficient of methyl acetate has been studied in detail by Lamble and Lewis (T., 1914, **105**, 2330), who found that the critical energy increment was about 17,000 calories per gram-molecule, which, on the quantum theory, would be provided by light of frequency of $\nu = 1{\cdot}6 \times 10^{14}$, or wave-length $\lambda = 1{\cdot}9\ \mu$ in the infra-red portion of the spectrum.

In a constant temperature enclosure, such as a thermostat, the density of the activating radiation, u_ν, is constant, and the most convenient method of causing an alteration in u_ν, and therefore of the reaction-velocity, is by alteration of the temperature. u_ν can, however, be altered by either decreasing or increasing the absorbable radiation density without altering the mean temperature. Thus plants which are photosensitive to the actinic part of the spectrum practically cease growing in the dark, although maintained at the same temperature, and other typical photochemical and photocatalytic reactions behave in like manner. In the case of infra-red radiation, however, it is difficult to shield any part of the reacting system from radiation of any particular absorbable frequency, since the system itself can emit this radiation either as a result of intramolecular vibration or even intermolecular collisions (see Nernst, "Die Theoretischen und Exp. Grundlagen des neuen Wärmesatzes," Halle, 1918, p. 63). Alteration of the medium in which the reacting molecules are dispersed does, however, produce an alteration in the reaction velocity, but, as pointed out above, it is at present uncertain whether this is the result of

an alteration in u_ν, the activating radiation density, or due to an alteration in ν equivalent to an alteration in the activating radiation frequencies and the mechanism of the reaction, or to both factors.

It is, however, quite possible to increase the density of the activating radiation, ν, by illumination with radiation of the correct wave-length, $\lambda = 1{\cdot}9\,\mu$. In the course of time, this radiation will be absorbed, and the energy will be equally distributed over the whole spectrum, resulting in an elevation of temperature, but if the reaction is truly photochemical and selectively absorbs radiation of this frequency, a marked acceleration in the reaction-velocity should result without an appreciable rise in temperature.

To test this point, a series of preliminary experiments was conducted on the rate of hydrolysis of methyl acetate dissolved in dilute hydrochloric acid and exposed to infra-red radiation; the velocity-coefficients obtained in this way were compared with the normal values obtained from identical solutions maintained in the dark.

Experimental.

As a source of infra-red radiation, preliminary experiments indicated that an arc lamp was unsuitable, since, although the carbon spectrum lines could be maintained at fairly uniform intensity, the infra-red portion of the spectrum (produced by the hot vapours) fluctuated in intensity. A uniform, although relatively feeble, infra-red beam was obtained from a small bundle of the oxide filaments commonly employed in the Nernst glow-lamp. A number of experiments were likewise conducted with a nichrome spiral raised to 600°; the relatively large quantity of non-radiant heat proved, however, to be a serious disadvantage. The sun was found to be the most convenient source of suitable radiation. In all cases, the spectrum was obtained by dispersion through a simple optical system of lenses and quartz prism, a salt prism not being available. No attempt was made to select any narrow spectral beam, but that part of the spectrum was employed commencing with the portion of the red just beyond the visible and stretching to an indefinite extent into the infra-red. To eliminate as far as possible the material absorption of the radiation, and thus minimise the dissipation of the energy as heat, the methyl acetate was illuminated directly with the radiation without the intervention of any glass. The solution undergoing hydrolysis was contained in a 100 c.c. beaker covered on the outside with tinfoil, a similar beaker containing the control solution.

Both beakers were maintained at uniform temperature by immersion in a thermostat or in broken ice and water. The temperature of each solution was continually observed, and samples for analysis withdrawn at simultaneous intervals for titration with 0·054*N*-baryta. In all respects, except for illumination, both solutions were maintained under identical conditions and treated in the same manner.

In the following tables are given the data of a number of experiments and the velocity-coefficients therefrom.

Illuminant: Nernst Filaments.

Acid: 0·1987*N*-HCl. k calculated as a unimolecular constant.

(I.)

Time.		Control.			Illuminated.		
Hrs.	Minutes.	Temperature.	Titre. C.c.	$k \times 10^4$.	Temperature.	Titre. C.c.	$k \times 10^4$.
1	55	21·75°	7·36	—	21·75°	7·36	—
2	9	—	7·50	12·71	—	7·76	36·79
2	39	21·75	8·22	23·16	21·80	8·54	36·81
3	4	—	8·34	22·46	—	8·64	25·77
4	15	21·75	8·80	14·10	21·80	8·83	14·39
5	25	—	9·48	15·07	—	9·50	15·24
∝		—	15·19	—	—	15·19	—

(II.)

12	46	20·9°	7·30	—	21·1°	7·20 (?)	26·00
12	58	22·3	7·34	7·39	22·3	7·45	31·67
1	14	23·4	7·37	6·00	23·7	7·65	41·35
1	31	23·7	7·45	9·26	23·85	8·00	41·09
1	46	24·9	8·01	25·22	24·7	8·38	41·69
				(Time 2 hrs. 4 mins.)			
2	14	24·5	8·16	26·54	24·2	8·57	—
3	10	18·35	8·51	24·27	18·2	9·10	40·15
4	45	18·35	9·84 (?)	41·94	17·9	9·55	41·94
∝		—	11·40	—	—	11·40	—

(III.)

Time.		Titre. C.c.		Temperature.		$k \times 10^4$.	
Hrs.	Minutes.	Control.	Illuminated.	Control.	Illuminated.	Control.	Illuminated.
9	35	6·09	6·09	21·70°	21·70°	—	Dark.
9	49	6·26	6·25	21·70	21·70	19·66	19·66
10	7	6·50	6·57	21·30	21·30	20·04	26·22
10	49	7·08	7·38	21·20	21·25	22·99	30·83
11	49	7·31	7·67	20·75	20·75	16·42	18·21
1	0	8·46	8·79	20·75	20·80	23·39	27·78
∝		12·21	12·21	20·75	20·75	—	—

Illuminant: Sunlight.

Time.		Temperature.		Titre. C.c.		$k \times 10^4$.		
Hrs.	Minutes.	Control.	Illuminated.	Control.	Illuminated.	Control.	Illuminated.	Remarks.
1	28	1·0°	1·0°	7·20	7·20	—	—	—
1	39	0·5	0·5	7·22	7·23	4·99	8·47	—
1	51	0·0	0·0	7·23	7·25	4·46	5·82	—
2	3	0·0	0·0	7·26	7·30	4·39	6·85	—
2	13	0·0	0·0	7·28	7·31	4·34	6·28	Sun clouded.
2	29	0·0	0·0	7·30	7·35	4·23	6·26	—
2	51	1·0	1·0	7·34	7·38	4·34	5·75	Sun clouded.
3	52	4·0	4·0	7·48	7·54	4·39	5·47	—
∞		—	—	11·06	11·06	—	—	—

Illuminant: Sunlight and Nichrome Coil.

Time.		Temperature.			Titre. C.c.		
Hrs.	Minutes.	Control.	Sun.	Nichrome.	Control.	Sun.	Nichrome.
1	50	4·0°	4·0°	14·0°	7·10	7·10	7·10
2	3	2·0	4·0	11·0	7·13	7·15	7·17
2	12	1·5	2·5	11·5	7·18	7·28	7·35
2	23	1·5	2·5	11·0	7·23	7·28	7·37
2	53	1·5	2·5	11·0	7·25	7·30	7·62
3	14	1·5	2·5	11·0	7·25	7·30	7·67
6	9	1·5	2·5	11·0	7·70	7·81	8·49
∞		—	—	—	13·29	13·29	13·29

Time.		$k \times 10^4$.			Nichrome calculated on temperature basis.
Hrs.	Minutes.	Control.	Sun.	Nichrome.	
1	50	3·84	—	—	—
2	3	4·89	12·21	18·97	9·02
2	12	4·93	12·29	18·49	12·23
2	23	3·80	7·41	13·48	11·90
2	53	2·37	5·34	13·82	9·19
3	14	4·05	3·34	9·61	5·73
6	9	—	4·85	10·12	5·27

It is evident that the illuminated methyl acetate is hydrolysed much more rapidly than that maintained at the same temperature in the dark.

That the variability in the velocity-coefficient of the illuminated reactants is chiefly due to an alteration in the intensity of the infra-red radiation was evident from the obvious alteration in the intensity of the sunlight by the passage of clouds. To control this factor, experiments were conducted in which the rate of liberation of iodine by catalytic atmospheric oxidation from acidified potassium iodide was simultaneously measured. This reaction is a typical photochemical one. It is evident from the following figures that the same factor, namely, the radiation intensity, affects both reactions, an alteration in the velocity-coefficient of one reaction coinciding approximately with a similar alteration in the other.

Illuminant: Sun.

Time. Hrs.	Time. Mins.	Titre. C.c. Control.	Titre. C.c. Illuminated.	Temperature. Control.	Temperature. Illuminated.	$k \times 10^4$. Control.	$k \times 10^4$. Illuminated.	Milligram of iodine liberated per minute.	Remarks.
1	38	5·90	5·90	9·0	9·0	3·32	3·32	—	Both dark.
1	53	5·93	5·93	3·0	3·5	3·33	7·61	0·0053	Both dark.
2	9	5·96	6·03	0·5	0·5	3·66	6·63	0·0023	Illuminated.
2	23	6·00	6·08	0·5	0·5	3·66	5·53	0·0043	—
2	40	6·03	6·10	0·5	0·5	3·36	—	—	—
3	1	6·06	6·16	2·0	2·0	—	5·47	0·0045	—
3	22	6·11	6·20	1·0	1·0	3·47	5·03	0·0026	—
3	41	6·13	6·23	1·0	0·5	3·21	4·48	—	—
8		9·73	10·90	—	—	—	—	—	—
1	12	5·88	5·82	6·0	9·0	2·78	3·49	—	Dark.
1	26	5·90	5·85	1·0	3·0	2·69	12·90	0·0014	Illuminated.
1	46	5·93	6·05	1·0	1·0	2·48	9·93	0·0036	—
2	2	5·95	6·08	1·0	0·5	3·68	6·51	0·0033	—
2	17	6·02	6·11	1·0	1·0	3·05	6·51	—	—
2	31	6·02	6·10	1·0	1·0	2·94	6·76	0·0164	—
2	46	6·05	6·17	1·0	1·0	—	—	—	—
8		11·60	11·14	—	—	—	—	—	—

Illuminant: Sun. Temperature, 0°.

Time.		Control.		Illuminated.		Milligram of iodine liberated per minute.
Hrs.	Mins.	Titre. C.c.	$k \times 10^4$.	Titre. C.c.	$k \times 10^4$.	
2	35	5·75	1·87	5·75	—	—
2	51	5·77	2·06	5·85	9·92	0·0043
3	8	5·81	3·70	5·86	4·11	0·0025
3	33	5·88	4·36	5·90	4·39	0·0025
3	51	5·95	—	5·97	5·99	0·0030
∝		11·85	—	11·85	—	—

It seemed possible that the radiation, falling on the surface of the methyl acetate solution, would produce a local rise of temperature, and that the heat would be carried by conduction to the walls of the vessel before the whole body of the solution acquired a higher temperature; thus local rapid hydrolysis might be produced. This possibility was, in reality, remote, since the solution was frequently agitated, and no difference in temperature was observed. Nevertheless, it was thought desirable to test this point experimentally. A small vessel containing oil, which could be maintained at any desired temperature by means of an electric resistance immersed in it, was lowered just under the surface of the methyl acetate solution, and sufficient energy was supplied to the oil to maintain the methyl acetate about 0·5° higher than the control experiment.

The velocity-coefficients obtained in this way agreed very closely with those calculated from the control experiments after correction for a rise in temperature of 0·6°, as is evidenced from the following values:

$k \times 10^4$ observed	2·13	3·98	3·73	3·92	3·96
$k \times 10^4$ calculated.....	2·13	3·99	3·73	3·86	3·96

From these experiments, it would seem that the hydrolysis of methyl acetate is in reality accelerated by irradiation in the infra-red portion of the spectrum, an interesting example of infra-red photochemical action; furthermore, that this spectral region is the region of activity anticipated by the application of the activation and quantum theories to chemical change.

It is hoped to continue and extend these experiments in the near future in order, if possible, to elucidate the mechanism of the catalytic activity of the acid employed. There are two tenable theories to explain this catalytic activity, either by an increase in the activating radiation density or by an alteration in the mechanism of the reaction.

Although the above experimental data, limited to one acid concentration, are too limited to draw any definite conclusion, it would appear probable that the second hypothesis, namely, an alteration

in the mechanism of the reaction, that is, the intermediate-compound theory of catalysts, is the correct one.

It will be noted that during the first period of illumination there is a very remarkable increase in the velocity-coefficient, and that subsequently the rate of reaction diminishes to a fairly constant value, which is, however, still greater than that of the unilluminated sample.

This phenomenon is not readily intelligible on the assumption of the action of the acid as affecting a simple increase in the radiation density, since a further increase in the radiation density should increase the reaction velocity *pro rata*. On the intermediate-compound theory, however, the observed result is to be anticipated.

Briefly, if the two reactions be represented by the following purely hypothetical equations:

$$\text{(i)}\quad CH_3\cdot CO_2Me + H_2O \rightleftharpoons MeOH + CH_3\cdot CO_2H$$

$$\text{(ii)}\quad CH_3\cdot CO_2Me + HCl + H_2O \rightleftharpoons CH_3\cdot CO_2Me,HCl,H_2O$$

$$CH_3\cdot CO_2Me,HCl,H_2O \rightleftharpoons MeOH + CH_3\cdot CO_2H + HCl.$$

the rate of decomposition in each case being unimolecular in excess of water, then the first reaction-velocity is governed by the rate of activation of the methyl acetate to react with the active water, and the second by two reactions, namely, the rate of activation of the methyl acetate to react with active hydrochloric acid, and by the rate of activation of the complex to break down into the products of the reaction. The rate of any sequent reaction is always governed by the slowest of the intermediate reactions; thus, if we assume the slowest one in this case to be the decomposition of the complex, then illumination with a particular frequency of light will accelerate the decomposition of the complex, so that the reaction-velocity will then be governed by the next slowest reaction, which we have assumed to be the combination of the methyl acetate and hydrated hydrochloric acid. This reaction, however, takes place more rapidly than the combination of methyl acetate and water. On this hypothesis of series reactions, the primary acceleration on illumination is to be attributed to the rapid decomposition of the complex, which is present in relatively large quantities, since it breaks down but slowly; the primary accelerates, then falls off until the normal rate of the next slowest reaction sets in.

Summary.

Preliminary experiments have indicated that the hydrolysis of methyl acetate is catalytically accelerated by infra-red radiation.

The spectral region of photoactivity is in agreement with that calculated on the activation and quantum theories of chemical action.

The experimental data obtained are most readily interpreted on the intermediate-compounds hypothesis in the case of the hydrolysis of esters by dilute acids. It is proposed to extend these experiments in order to obtain further information as to the number and nature of these intermediate compounds, and to examine the spectral region of their activation in more detail.

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CXL.—*The Action of Chlorine on* 3 : 5-*Dichloro*-1 : 1-*dimethyl*-$\Delta^{2:4}$-cyclo*hexadiene.*

By LEONARD ERIC HINKEL.

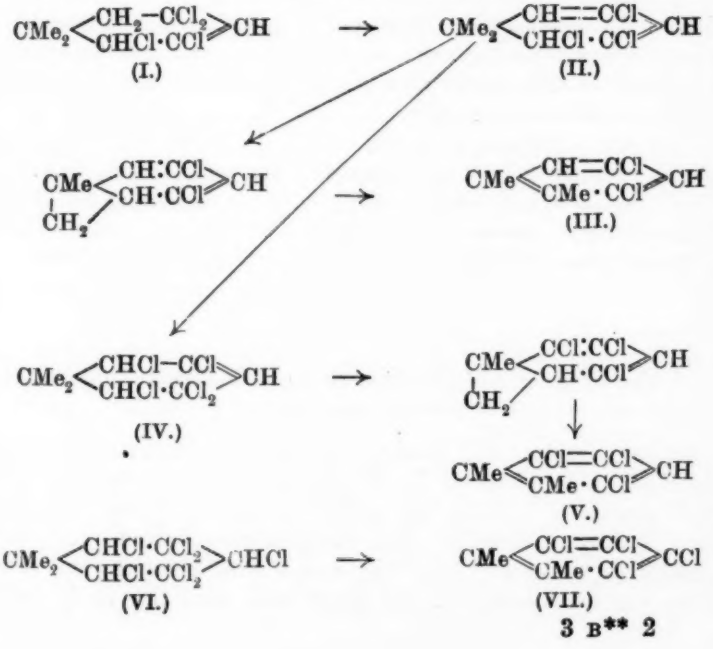
IN the study of the conversion of hydroaromatic derivatives into compounds of the aromatic series, the action of bromine on 3 : 5-dichloro-1 : 1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene was fully investigated (Crossley, T., 1904, **85**, 264). It was shown that the reaction was largely influenced by condition of experiment, 2 molecules of bromine giving rise to a viscid liquid, which, on distillation, gave 3 : 5-dichloro-4-bromo-*o*-xylene and a crystalline solid, $C_8H_9Cl_2Br_3$, presumed to be dichlorotribromodimethyl*cyclo*hexene,

$$CMe_2\begin{<}CHBr\cdot CClBr\\ CH{=}{=}{=}CCl\end{>}CHBr.$$

On the other hand, 1 molecule of bromine gave as principal product 3 : 5-dichloro-6-bromo-*o*-xylene. Explanations of the production of the various substances are suggested in the original paper, but as several points remained to be cleared up, the work was repeated, using chlorine instead of bromine, in the hope that more light would be thrown on the mechanism of this type of reaction.

When 3 : 5-dichloro-1 : 1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene is treated with chlorine, the product consists of a viscous syrup, which yields a small quantity of a crystalline solid, $C_8H_9Cl_5$. The syrupy filtrate from the crystals yields, on distillation, the two isomeric trichloro-*o*-xylenes, and also tetrachloro-*o*-xylene. The compound $C_8H_9Cl_5$ is evidently a *pentachlorodimethyl*cyclo*hexene*, corresponding with and formed in a manner similar to the dichlorotribromodimethyl*cyclo*hexene described by Crossley (*loc. cit.*), and in like manner accounts for the formation of 3 : 4 : 5-trichloro-*o*-xylene in

the filtrate from the crystals, since the pentachloro-compound decomposes on heating into 3 : 4 : 5-trichloro-*o*-xylene. The formation of pentachlorodimethyl*cyclo*hexene does not, however, account for the production of either 3 : 5 : 6-*trichloro*-o-*xylene* or tetrachloro-*o*-xylene. The action of chlorine on dichlorodimethyl*cyclo*hexadiene must be more deep-seated, since 100 grams of the latter yield only 28 grams of pentachlorodimethyl*cyclo*hexene, 18—20 grams of 3 : 5 : 6-trichloro-*o*-xylene, and 10—12 grams of a mixture of 3 : 4 : 5-trichloro-*o*-xylene and tetrachloro-*o*-xylene. Moreover, when 1 molecule of chlorine acts on dichlorodimethyl*cyclo*hexadiene, the resulting liquid always contains a considerable quantity of the unchanged original compound, together with 3 : 5-di- and 3 : 5 : 6-tri-chloroxylenes; the yield of 3 : 5 : 6-trichloro-*o*-xylene is small, being only 16—18 grams from 100 grams of dichlorodimethyl*cyclo*hexadiene. The product of the action of one molecular proportion of chlorine on dichlorodimethyl*cyclo*hexadiene is probably tetrachlorodimethyl*cyclo*hexene (I); this substance is unstable, and very readily evolves hydrogen chloride even at low temperatures, probably forming a trichlorodimethyl*cyclo*hexadiene (II), which then slowly loses another molecule of hydrogen chloride, yielding 3 : 5-dichloro-*o*-xylene (III). A compound of formula II would combine with 1 molecule of chlorine in a manner similar to dichlorodimethyl*cyclo*hexadiene, yielding



an unstable substance (IV), from which, by loss of 1 molecule of hydrogen chloride, 3:5:6-trichloro-*o*-xylene (V) would result.

The formation of tetrachloro-*o*-xylene can be explained by supposing that with excess of chlorine the two compounds II and IV are successively formed, and that more chlorine combines with IV, yielding an unstable substance having the formula VI, which immediately loses hydrogen chloride, giving rise to tetrachloro-*o*-xylene (VII).

The only point to be decided is the position of the chlorine atoms in the two possible trichloro-*o*-xylenes. 3:4:5-Trichloro-*o*-xylene was therefore synthesised from *o*-4-xylidene, which was chlorinated, and the amino-group then displaced by chlorine. The 3:4:5-trichloro-*o*-xylene obtained in this way melted at 96°, and its melting point remained unchanged when mixed with the substance obtained by heating pentachlorodimethyl*cyclo*hexene. Consequently, the other trichloro-*o*-xylene must have the chlorine atoms in the 3:5:6-position.

Both the trichloro-*o*-xylenes yield on further chlorination the same tetrachloro-*o*-xylene, melting at 223—224°, which was identical with the compound obtained by the action of nitric acid on pentachlorodimethyl*cyclo*hexene, and also with the substance, melting at 223—224°, isolated in the distillate obtained from the filtrate from pentachlorodimethyl*cyclo*hexene.

3:4:5-Trichloro-*o*-xylene on bromination readily yields 3:4:5-*trichloro*-6-*bromo*-*o*-*xylene*, but on brominating 3:5:6-trichloro-*o*-xylene in a similar manner, an unexpected reaction takes place, giving rise to 3:5-dichloro-4:6-dibromo-*o*-xylene, and not 3:5:6-trichloro-4-bromo-*o*-xylene.

Both the trichloro-*o*-xylenes resemble the dichlorobromo-*o*-xylenes in their behaviour towards nitric acid. Thus, 3:4:5-trichloro-*o*-xylene gives with fuming nitric acid 3:4:5-*trichloro*-6-*nitro*-*o*-*xylene*, whereas 3:5:6-trichloro-*o*-xylene under similar treatment gives 3:5-dichloro-4:6-dinitro-*o*-xylene.

Experimental.

Action of Excess of Chlorine on 3:5-*Dichloro*-1:1-*dimethyl*-$\Delta^{2:4}$-cyclo*hexadiene*.

Seventy grams of freshly prepared dichlorodimethyl*cyclo*hexadiene were dissolved in 70 grams of dry chloroform, and a rapid stream of chlorine was passed in, the whole being cooled in ice. Hydrogen chloride was immediately evolved, and subsequently in torrents. After saturation with chlorine, the chloroform was evaporated on the water-bath, and the viscid, yellow

liquid was placed in a vacuum over sodium hydroxide, when it gradually deposited colourless crystals. These were collected (18·5 grams) (filtrate = *A*), and, after being rapidly washed with light petroleum, purified by crystallisation from alcohol (Found: Cl = 62·62. $C_8H_9Cl_5$ requires Cl = 62·83 per cent.).

2:3:3:4:5-*Pentachloro*-1:1-*dimethyl*-Δ^5-cyclo*hexene*,

$$CMe_2\begin{<}CHCl\cdot CCl_2\\CH=CCl\end{>}CHCl,$$

is readily soluble in the cold in ether, chloroform, acetone, benzene, or methyl and ethyl alcohols, and in light petroleum on warming. It crystallises in stout, prismatic needles melting at 103·5°.

*Action of Heat on Pentachlorodimethyl*cyclo*hexene.*

The substance was heated at 120—130° in a sulphuric acid bath, when it melted to a colourless liquid, and copious evolution of hydrogen chloride occurred. The liquid was then removed from the acid-bath and heated more strongly until no further evolution of hydrogen chloride occurred and the liquid began to boil. The residue solidified on cooling, and was crystallised from alcohol (Found: Cl = 51·16. Calc.: Cl = 50·83 per cent.).

3:4:5-Trichloro-*o*-xylene is very readily soluble in ether, chloroform, benzene, light petroleum, or hot alcohol, crystallising from the latter in masses of felt-like needles, which, on pressing, form a waxy mass melting at 96°. It distils unchanged at 261°, is volatile in steam, and is evidently identical with the compound described by Claus and Kautz (*Ber.*, 1885, **18**, 1369), who give m. p. 93° and b. p. 265°.

On chlorination and bromination in the presence of iron, it gives, respectively, 3:4:5:6-tetrachloro-*o*-xylene melting at 223—224° (p. 1300) and 3:4:5-trichloro-6-bromo-*o*-xylene melting at 226° (p. 1300). Fuming nitric acid converts it into 3:4:5-trichloro-6-nitro-*o*-xylene melting at 149° (p. 1301).

*Action of Nitric Acid on Pentachlorodimethyl*cyclo*hexene.*

Five grams of the *cyclo*hexene derivative were heated with 40 c.c. of fuming nitric acid over a water-bath. A vigorous action ensued, and, after heating for ten minutes, the contents of the flask were poured into cold water. The pasty solid was collected, washed with water, and, after three crystallisations from ethyl acetate, the needles melted at 223—224°; the melting point was not altered on mixing with 3:4:5:6-tetrachloro-*o*-xylene (p. 1300) (Found: Cl = 58·4. Calc.: Cl = 58·19 per cent.).

Examination of Filtrate A (p. 1299).

The liquid was heated in a distilling flask to 140° and gradually raised to 180°; a copious evolution of hydrogen chloride occurred. The liquid was maintained at 180—200° for one hour, and then gently distilled, three main fractions being obtained boiling at 225—245°, 245—260°, and 260—270°. The first two fractions, which partly solidified on keeping, were subjected to careful and repeated fractional distillation, and the main fraction, b. p. 230—240°, solidified completely, on cooling, to a colourless, crystalline mass, which, after being crystallised several times from alcohol, melted sharply at 47·5°, and consisted of 3:5:6-*trichloro*-o-*xylene* (p. 1302) (Found: Cl = 50·99. $C_8H_7Cl_3$ requires Cl = 50·83 per cent.).

The residue of higher boiling point was added to the third fraction (b. p. 260—270°), and on submitting the mixture to repeated fractional distillation, two main fractions, b. p. 255—265° and 275—280°, were obtained. These were subjected to repeated fractional crystallisation from alcohol, and then from ethyl acetate, in which the fraction of higher boiling point is less readily soluble, and a partial separation was effected yielding two substances, one crystallising from alcohol in felt-like needles melting at 96°, and at the same temperature when mixed with 3:4:5-trichloro-*o*-xylene (p. 1299), the other crystallising from ethyl acetate in long, transparent needles melting at 223—224°, and at the same temperature when mixed with 3:4:5:6-tetrachloro-*o*-xylene (below).

Action of Chlorine on 3:4:5-*Trichloro*-o-*xylene: Formation of* 3:4:5:6-*Tetrachloro*-o-*xylene* (VII).

Two grams of the substance were dissolved in 10 c.c. of dry chloroform, and chlorine was rapidly passed into the solution in the presence of a small quantity of iron filings. On warming, substitution readily took place. The chloroform was evaporated and the residue crystallised from ethyl acetate. The substance is very readily soluble in ether, and readily so in chloroform, hot alcohol, or ethyl acetate, crystallising from the latter in long, slender, glistening needles melting at 223—224° (Claus and Kautz, *loc. cit.*, give 215°).

Action of Bromine on 3:4:5-*Trichloro*-o-*xylene: Formation of* 3:4:5-*Trichloro*-6-*bromo*-o-*xylene.*

The substance was dissolved in a small quantity of chloroform, and bromine added in the presence of iron filings. On warming,

substitution took place, and the sparingly soluble bromo-derivative separated. The chloroform was evaporated and the residue dissolved in benzene, the solution being washed with water, dried, concentrated, and allowed to crystallise (Found: Cl = 36·67; Br = 28·05. $C_8H_6Cl_3Br$ requires Cl = 36·92; Br = 27·73 per cent.).

The compound is readily soluble in ether or benzene, sparingly so in chloroform or alcohol, and crystallises from ethyl acetate in slender, glistening needles melting at 226°.

Action of Nitric Acid on 3 : 4 : 5-*Trichloro-o-xylene: Formation of* 3 : 4 : 5-*Trichloro*-6-*nitro-o-xylene.*

Four grams of the substance were gradually added to 40 c.c. of fuming nitric acid and warmed on the water-bath for twenty minutes, when the solid gradually dissolved. The mixture was poured into water, and the separated solid crystallised from alcohol, in which it is sparingly soluble (Found: N = 5·436. $C_8H_6O_2NCl_3$ requires N = 5·5 per cent.).

The compound is readily soluble in ether, acetone, benzene, chloroform, or light petroleum, and moderately so in hot alcohol or hot glacial acetic acid; it crystallises from alcohol in stout, transparent crystals possessing a slight yellow tinge, and melting at 149°.

Synthesis of 3 : 4 : 5-*Trichloro-o-xylene.*

o-4-Xylidine was acetylated and chlorinated as described by Crossley (*loc. cit.*). Three grams of the resulting 3 : 5-dichloro-*o*-4-xylidine were suspended in 15 c.c. of concentrated hydrochloric acid, in which it is not soluble in the cold, a solution of 1·5 grams of freshly prepared cuprous chloride in 15 c.c. of concentrated hydrochloric acid was added, and a solution of 1·1 grams of sodium nitrite in the least amount of water dropped into the mixture, which was heated on a water-bath to 60—70°. After one hour, the whole was distilled in a current of steam, when a solid passed over which melted at 82°. After recrystallising twice from alcohol, the crystals melted sharply at 96°, and the melting point was not changed when the substance was mixed with the trichloro-*o*-xylene described on p. 1299.

Action of One Molecular Proportion of Chlorine on 3 : 5-*Dichloro*-1 : 1-*dimethyl*-$\Delta^{2:4}$-*cyclohexadiene.*

Dichlorodimethyl*cyclo*hexadiene (1 mol.) was dissolved in twice its weight of dry chloroform, and the solution cooled in a freezing mixture of ice and salt. Chlorine was passed into the mixture,

and the hydrogen chloride, which was immediately evolved, absorbed in a soda-lime tube. The passage of chlorine was stopped when the increase in total weight of the apparatus was equivalent to one molecular proportion of chlorine. On evaporating the chloroform, a pale yellow liquid remained which showed no signs of crystallisation, even after remaining for a long time in a vacuum over sodium hydroxide. The liquid was heated to 150—180° for one hour, when much hydrogen chloride was evolved. The liquid was then distilled, and a clear, yellow liquid, boiling between 215° and 241°, passed over. The liquid was submitted to careful and repeated fractional distillation, and three fractions, boiling at 217—220°, 222—226°, and 228—233°, were collected.

Fraction b. p. 217—220°.—This liquid, when left in the air, rapidly darkened and resinified, and when hydrolysed with 30 per cent. sulphuric acid yielded dimethyldihydroresorcin, showing that it contained 3:5-dichloro-1:1-dimethyl*cyclo*hexadiene.

Fraction b. p. 222—226°.—This liquid could not be separated into a portion boiling constantly at 226° (3:5-dichloro-*o*-xylene). When treated with bromine in the presence of iron filings, it gave 3:5-dichloro-4:6-dibromo-*o*-xylene, which, after crystallisation from ethyl acetate, melted at 233° (compare Crossley, *loc. cit.*, p. 284), and on nitration gave 3:5-dichloro-4:6-dinitro-*o*-xylene melting at 173—174°, and identical with the compound obtained by the action of nitric acid on 3:5:6-trichloro-*o*-xylene (p. 1303).

Fraction b. p. 228—233°.—The liquid almost entirely solidified on cooling. The crystals were collected and the filtrate was dissolved in warm alcohol, and the solution cooled in ice, when a further yield of crystals was obtained, which, after crystallising several times from alcohol, melted at 47·5°. This melting point was not altered when the substance was mixed with 3:5:6-trichloro-*o*-xylene (p. 1300).

3:5:6-*Trichloro*-o-*xylene* is readily soluble in the cold in ether, benzene, chloroform, light petroleum, or ethyl acetate, crystallises from methyl or ethyl alcohol in short, colourless crystals, and can be distilled unchanged. It is readily acted on by chlorine in the presence of iron filings; the solid product crystallises from ethyl acetate in long, glistening needles melting at 223—224°, and is identical with 3:4:5:6-tetrachloro-*o*-xylene (p. 1300).

Action of Bromine on 3:5:6-*Trichloro*-o-*xylene.*

Two grams of the substance were dissolved in 10 c.c. of dry chloroform, and excess of bromine was added in the presence of iron filings. On warming, substitution takes place readily. The

solid product crystallised from ethyl acetate in long, silky needles melting at 233°, and this melting point was not changed when the substance was mixed with 3:5-dichloro-4:6-dibromo-*o*-xylene (Found: Cl = 21·65; Br = 47·63. Calc.: Cl = 21·32; Br = 48·05 per cent.).

Action of Nitric Acid on 3:5:6-Trichloro-o-xylene.

Five grams of the substance were slowly added to 30 c.c. of fuming nitric acid and warmed on the water-bath, when the solid dissolved, after which a rather vigorous action took place. The heating was continued for twenty-five minutes, the mixture poured into cold water, and the separated semi-solid, after being washed with warm water, crystallised from alcohol. Considerable difficulty was experienced in purifying this material by means of alcohol, and it was therefore twice recrystallised from light petroleum (b. p. 40—60°) and finally from alcohol. The flat plates obtained in this way melted at 174°, and were identified as 3:5-dichloro-4:6-dinitro-*o*-xylene (Crossley, *loc. cit.*, p. 284) (Found: N = 10·51. Calc.: N = 10·56 per cent.).

The author wishes to express his indebtedness to Colonel A. W. Crossley, C.M.G., for suggesting the above investigation and for much valuable help and advice throughout; thanks are also due to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the expenses of this investigation.

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CXLI.—*The Effect of Asymmetry. A Study in Crystal Structure.*

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COMPARATIVE studies of more or less closely related organic compounds abound in the literature of crystallography; in fact, the attempt to trace so-called "morphotropic resemblances" may be regarded as one of the distinctive features of crystallographic investigation during the last fifty years. Whilst such investigations have added extensively to the general stock of knowledge, they cannot, unfortunately, be said to have led to the formula-

tion of any general laws correlating chemical composition and crystalline form. At least one of the causes of this general failure has been recently revealed as the result of the investigation of crystal structure by means of *X*-rays. It is now clear that the Bravais space-lattices do not always represent completely the structure of a crystal, for something like 70 per cent. of the structures already elucidated by *X*-ray methods consist of several interpenetrating space-lattices, that is, of "point systems" in the sense of Sohncke, Fedorov, and Schönflies. Crystal structure is thereby proved to be a subject of great complexity, and much further investigation is evidently needed before general laws can be formulated.

The object of the present research was to ascertain whether a definite similarity may exist between the crystalline forms of two closely related organic substances, one of which differs from the other in possessing an asymmetric atom. The kind of similarity sought was of that definite degree which exists between isomorphous substances rather than that vaguely implied by a "morphotropic resemblance."

In selecting materials for examination, it was necessary to find a series of compounds in which the replacement of one radicle by another is not incompatible with an isomorphous relationship (at least so long as the molecule remains symmetrical) before proceeding to inquire whether a further replacement of radicles, by which the molecule becomes asymmetric, is compatible with the survival of isomorphism. Now, experience shows that in series involving the replacement of organic radicles, isomorphism is only to be found where the molecule is relatively large in proportion to the change of composition, and it therefore seemed probable that compounds of the type R_4NHgI_3 (that is, "double compounds" of a quaternary ammonium iodide with mercuric iodide in the ratio 1:1), in which R may represent either identical or different organic radicles, should be suitable for the end in view. Such compounds, having a pale to deep lemon-yellow colour, are known to crystallise well from acetone solutions. A commencement was therefore made with a series of compounds in which R_4 is wholly represented by alkyl groups (compare table I), but no definite cases of isomorphism were encountered. This is a fact of some significance, as illustrating the highly sensitive character of the relationship between form and composition: in spite of the high molecular weight, the replacement of even a single methyl by an ethyl radicle brings about a fundamental change of crystalline form and structure.

The investigation of a still more complex group then became necessary. The phenylalkylammonium compounds, of the general

TABLE I.

*The Alkylammonium Group of Compounds.**

No.	Substance.	System.	Crystallographic constants. $a:b:c$.	Axial angles.	Prism angle.	Cleavage.
1	Me_4NHgI_3	Rhombic	0·5777 : 1 : 0·5199	—	60° 2′	(001) imperfect.
2	$MeEt_3NHgI_3$	Anorthic	1·1202 : 1 : 0·5578	$\alpha=102°55'$ $\beta=93°56'$ $\gamma=108°25'$	98°18′	(110) good. (1$\bar{1}$0) good.
3	Et_4NHgI_3	Monoclinic	1·4826 : 1 : 0·8192	$\beta=107°55'$	109°20′	(100) perfect. (001) imperfect.
4	$PrEt_3NHgI_3$	,,	1·1350 : 1 : 0·7359	$\beta=97°11'$	96°48′	(110) perfect.
5	$MePr_3NHgI_3$	,,	1·0749 : 1 : 0·6542	$\beta=93°22'$	94° 2′	(011) fair. (110) imperfect.
6	$EtPr_3NHgI_3$	Rhombic	0·6890 : 1 : 0·5106	—	69° 8′	(011) perfect. (110) imperfect.
7	Pr_4NHgI_3	Monoclinic	1·4965 : 1 : 0·7328	$\beta=113°16'$	107°56′	($\bar{2}$01) good.

* The corresponding trimethylethyl and trimethylpropyl compounds were also prepared, but the crystals could not be obtained in a form suitable for measurement. In addition to the 1 : 1-compound, tetraethylammonium iodide also forms an orange-coloured substance with mercuric iodide in the molecular proportions 2 : 3. A description of this compound is included in the experimental part (p. 1314).

formula $R_3PhNHgI_3$, furnished clear cases of isomorphism. In the annexed table, the first member is not isomorphous with the succeeding compounds. The next three compounds, however, are clearly isomorphous, and, moreover, exhibit the following peculiarity. Although the compound $Me_2EtPhNHgI_3$ (No. 9) differs from the compound $MeEt_2PhNHgI_3$ (No. 11) by an amount expressible by CH_2, it is much more closely isomorphous with it than is the compound $Me_2PrPhNHgI_3$ (No. 10), in spite of the fact that the last two compounds are isomerides. The similarity of angles between the first two mentioned compounds is, indeed, comparable with the close isomorphism met with in the sulphates of potassium, rubidium, cæsium, and ammonium. The isomorphism of the three compounds numbered 9—11 was confirmed by a method which has been especially developed by one of us (T., 1906, **89**, 1120). Crystal fragments of any one of the three substances continue to grow when placed in a saturated solution of either of the others, and thus satisfy one of the most rigid tests for isomorphism. Proceeding with the table, it is seen that there is a marked change of form in passing from No. 11 to No. 12, differing in composition by CH_2, but that the two compounds $Et_3PhNHgI_3$ (No. 12) and $Et_2PrPhNHgI_3$ (No. 13), also differing by CH_2, are closely isomorphous—a conclusion which was confirmed by the formation of regular growths when a crystal of one is immersed in a saturated solution of the other.

The choice of the final materials was, of course, dictated by practical considerations. Asymmetry of molecular configuration is most easily produced by the inclusion of a benzyl radicle, and the phenylbenzylalkylammonium group of compounds, represented by the general formula $R_2(CH_2Ph)PhNHgI_3$, in which asymmetry is involved by the selection of different R-groups, was therefore examined. The results of the crystallographic examination are summarised in table III.

A glance at the values of the axial ratios is sufficient to show that the first substance has no really close relationship to the second and third compounds; moreover, the large discrepancy in the axial ratio $b:c$ of the fourth substance shows that it also stands alone. The relationships of the second and third compounds (No. 15 and No. 16 of the table) deserve further notice. The axial ratios and angle β differ by relatively small amounts, thus indicating the possibility that the two substances are isomorphous. A comparison of the form-development points the same way. In the methylethyl derivative we have $b\{010\}$, $a\{100\}$, $m\{110\}$, $c\{001\}$, $q\{011\}$, and $r\{\bar{2}01\}$, with the forms b and a developed as small facets, whilst in the diethyl derivative we have

TABLE II.

*The Phenylalkylammonium Group of Compounds.**

No	Substance.	System.	Crystallographic constants. $a : b : c$.	Crystallographic constants. β.	Prism angle.	Cleavage.
8	$Me_3PhNHgI_3$	Monoclinic	1·2400 : 1 : 0·6783	104°54′	100°18′	(100) good.
9	$Me_2EtPhNHgI_3$	,,	0·7391 : 1 : 0·6783	94° 6′	72°48′	(001) perfect.
10	$Me_2PrPhNHgI_3$	,,	0·7775 : 1 : 0·6711	96°34′	75°22′	(001) perfect.
11	$MeEt_2PhNHgI_3$	,,	0·7319 : 1 : 0·6976	93°24′	72°18′	(001) perfect. (110) imperfect.
12	$Et_3PhNHgI_3$	,,	1·1250 : 1 : 1·3490	101°21′	95°36′	(100) perfect.
13	$Et_2PrPhNHgI_3$	,,	1·1185 : 1 : 1·3440	100°57′	95°22′	(100) perfect. (110) imperfect.

* Phenyltriethylammonium iodide also forms a second type of compound with mercuric iodide in the molecular proportions 2 : 1. A description of this substance is included in the experimental part (p. 1318).

TABLE III.

The Phenylbenzylalkylammonium Group of Compounds.

No.	Substance.	System.	Crystallographic constants. $a : b : c$.	Crystallographic constants. β.	Prism angle.	Cleavage.
14	$Me_2(CH_2Ph)PhNHgI_3$	Monoclinic	0·7386 : 1 : 0·5105	92°26′	72°52′	(100) fair.
15	$MeEt(CH_2Ph)PhNHgI_3$	,,	0·9878 : 1 : 0·5797	106° 9′	87° 0′	(110) good.
16	$Et_2(CH_2Ph)PhNHgI_3$	,,	1·0301 : 1 : 0·6354	108° 7′	88°48′	(001) imperfect. ($\bar{2}$01) perfect.
17	$MePr(CH_2Ph)PhNHgI_3$	,,	1·1060 : 1 : 0·7766	102°55′	94°18′	(100).

the same forms, but without $b\{010\}$ and $a\{100\}$. Since in the former compound these two forms were but slightly developed, their absence in the latter has no particular significance, merely indicating that one compound tends to present a richer form-development than the other. The coincidence of all the remaining forms, and, more especially, the occurrence in common of the form $\{\bar{2}01\}$, point to an identical space-lattice, and prove the substances to be isomorphous, in so far as purely geometrical characters can do so. This conclusion is strengthened by the observation that a broken fragment of the diethyl compound, when placed in a saturated solution of the methylethyl derivative, immediately begins to grow, and eventually becomes a perfect crystal.

The sole remaining question relates to the special chemical nature of phenylbenzylmethylethylammonium mercuri-iodide: whether the crystals are dextro- and lævo-enantiomorphs, or are racemic or pseudo-racemic. As no trace of optical inhomogeneity was ever observed in crystals selected from various crops, and as the measurements gave no indications of the wide variations of angle characteristic of pseudo-racemic crystals, it follows that the crystals are either truly racemic or, on the other hand, a conglomerate of the two enantiomorphs. In order to decide this question, three of the largest crystals, weighing approximately 2, 1·5, and 1 gram respectively, were powdered, and as rapidly as possible dissolved separately in about 20 c.c. of acetone, and the solutions immediately examined in the polarimeter. In no case was an appreciable rotation observed; the crystals therefore presumably represent a true racemate. This conclusion was supported by etch-figures on the crystal faces, for they were in accordance with holohedral symmetry.

The main result of this investigation is to prove that racemic crystals of phenylbenzylmethylethylammonium mercuri-iodide are isomorphous with the corresponding diethyl derivative, although the racemic crystals contain two kinds of asymmetric molecules, whilst in the diethyl derivative all the molecules are necessarily identically similar and symmetrical.

Experimental.

Preparation of Compounds.

The general method of preparing the compounds was as follows. The proper molecular proportions of the tertiary amine, alkyl iodide, and mercuric iodide were warmed together with acetone until the whole was dissolved, and the solution allowed to remain overnight. Crystals were usually obtained the following day,

although two or three recrystallisations were sometimes necessary before really good crystals were formed.

Some of the compounds prepared were found to be unsuitable for crystallographic investigation; the trimethylethyl and trimethylpropyl compounds, for example, crystallise in needles. On the other hand, in some cases more than one compound is formed; thus, tetraethylammonium iodide unites with mercuric iodide in the proportions 1:1 and 2:3. With regard to the phenylalkyl group, it was observed that increase of molecular weight lowered the crystallisability of the compounds; sometimes five or six recrystallisations were necessary before sufficiently good crystals were obtained. The phenyldimethylpropyl and phenyldimethylethyl compounds have a strong tendency to form needles, but after repeated recrystallisations they finally yielded some measurable crystals. In one and the same solution, phenyltriethylammonium iodide forms with mercuric iodide two compounds, which on analysis proved to be the 2:1- and 1:1-compounds respectively; these were separated by hand. In the phenylbenzylalkyl group, the chemical combination of the various components was relatively slow; several attempts to prepare phenylbenzylethylpropylammonium mercuri-iodide were made, but a pure product could not be isolated.

Method of Analysis.

The method employed for the quantitative estimation of the mercury was that described by Marsh and Lye (*Analyst*, 1917, **42**, 84). The process is a modification of the method of estimating mercury by combustion with quicklime. Calcium oxalate is placed at the closed end of the tube, and after this a few grams of dry calcium sulphate and quicklime; next comes about 1 gram of the substance ground up with about the same weight of potassium cyanide and a few grams of calcium sulphate and quicklime.* After this, 5 or 6 grams of a mixture of calcium sulphate and quicklime are packed in, and the remainder of the tube is filled with quicklime. The vaporised mercury is collected in a small flask of water. No calcium sulphate was used with the tetramethyl, phenyldimethylpropyl, and phenyldiethylpropyl compounds. It may be noted that more satisfactory results were obtained with a tube longer than that recommended by Marsh and Lye; the length of the tube before drawing out should be about 50 cm.

* In the case of the phenylbenzylalkylammonium group about a gram of black copper oxide was mixed with the substance and the potassium cyanide was placed nearer the drawn-out end of the tube.

Method of Crystallographic Examination.

A Fedorov two-circle goniometer was exclusively employed in the measurement of the crystals. Apart from its other advantages, a two-circle instrument is especially useful for the measurement of laboratory products, the crystals of which are frequently of microscopic dimensions, since it necessitates only one adjustment of the crystal. The results were plotted on a Fedorov stereographic net, and the crystal system, if not immediately obvious, was deduced from zonal angles, graphically determined by the help of the three-point compass and stereographic net, and later confirmed by an examination of the optical properties. The crystallographic indices were determined graphically in every case by the help of the gnomonic projection. In order to avoid possible errors, the axial ratios have been calculated in two independent ways for every compound. First, by the method in common use, depending on the solution of spherical triangles, and, secondly, by Goldschmidt's method (*Zeitsch. Kryst. Min.*, 1893, **21**, 210), based on the gnomonic projection. The crystal drawings were made directly from the gnomonic projection by the method devised by Goldschmidt (*Zeitsch. Kryst. Min.*, 1891, **19**, 352). Attention is especially called to this point, because the method does not appear to have come into general use, although experience proves it to be superior to all the other methods of drawing crystals.

In the descriptions of the crystals, the conventional rules have been adopted [in the monoclinic system, for instance, the indices (010) have been uniformly assigned to the plane of symmetry]; but, in addition, the "correct setting" of the crystal according to Fedorov's methods, and his "complex-symbol," have been worked out in every case, and the "transformation equations," by which the indices corresponding with Fedorov's theoretical ideas may be obtained from the conventional indices, are also given. The descriptions consequently contain everything necessary for an absolute identification of any of the compounds on any future occasion by the method now generally known as "crystallochemical analysis," a descriptive outline of which has already been given elsewhere (*Ann. Reports*, 1913, **10**, 245; 1914, **11**, 248; 1917, **14**, 227). An explanation of the meaning of the terms "transformation equations" and "complex-symbol" may well be appended here, as not having been previously given.

The connexion between the indices representing any face of a crystal when referred to two different sets of axes is most conveniently expressed by means of "transformation equations," by which one set of indices can be immediately deduced from the

other. Thus, in the case of the anorthic methyltriethylammonium mercuri-iodide (p. 1313), the new indices (pqr) of any face referred to the axes chosen by Fedorov on structural grounds can be obtained from its indices (hkl) when referred to the conventional axes by the equations: $p=-1h+0k+2l$, $q=1h+0k+2l$, $r=1h+2k+0l$. The numerical coefficients of hkl in these equations are $\bar{1}02$, 102, and 120 respectively, and the equations can be abbreviated to "trans. $\bar{1}02/102/120$"—a form which is adopted in this paper.

The Fedorov "complex-symbol" is an expression which indicates simultaneously both the type of structural arrangement and the characteristic angles of the crystal (if necessary, after a suitable homogeneous deformation or shear). The initial term of the symbol is the number 6, 4, or 3, according as the crystal is held to approximate most closely to a hexagonal, tetragonal, or trigonal (rhombohedral) form respectively. When necessary, this number is immediately followed by a letter, h, o, or d, respectively indicating, in Fedorov's phraseology, that the arrangement is "hexahedral" (that is, that of a simple space-lattice), "octahedral" (that of a centred lattice), or "dodecahedral" (that of a face-centred lattice). Thus $4h$ signified that the type of the structural arrangement is that of a simple tetragonal space-lattice, whilst $3d$ indicates the face-centred trigonal lattice as being the structural type. All remaining terms of the complex-symbol are numerical constants, representing degrees of arc, which serve to characterise each crystal species. As described below, one of these numerical terms, expressing in general the value of the angle (after a shear) between the correct basal plane and primary pyramid, is especially important in Fedorov's classification, so by way of contrast he encloses in brackets all other terms as are necessary to express the angular deviations of the lattice from an ideal hexagonal, tetragonal, or trigonal form. Thus, in the symbol "$(6)37\frac{1}{2}(+3)$," the first term means that the crystal approaches ideal hexagonal symmetry, the second that the principal angle is $37\frac{1}{2}°$, and the third that the prism angle has the value $60°+3°$ instead of the value 60° proper to an ideal hexagonal lattice. The absence of any further term indicates that the system is orthorhombic. On the other hand, in the symbol "$(3h;+2)58(0)$" we have a new kind of numerical term, namely, $+2$, immediately following the structural term $3h$. This means that the angle between two of the structural planes is not 90°, but $90°+2°$, in other words, that the crystal is monoclinic with a value $\beta=92°$. The last term, "(0)," refers, as before, to the prism angle, and means that the deviation (from the ideal value of 60°) is nearer

0° than ½°. The angles in the complex-symbols are only given to the nearest half degree, since this is the limit of accuracy of the graphical methods employed.

The Fedorov complex-symbol derives its immense importance from two facts: first, unlike axial ratios, it is an unambiguous constant for each crystal-species, and, secondly, such symbols can be readily classified in ordered form. In his "Dictionary of the Crystal-Kingdom," the publication of which by the Petrograd Academy of Science has been delayed by circumstances beyond its control, the late Professor Fedorov has classified all the existing data. All crystals belonging to the same type (say 4*h* or 3*d*, and so on) are first brought together, and then arranged in order according to the value of the principal angle mentioned above. Any well-developed crystalline substance which has once been measured, and placed in the dictionary in the place required by its complex-symbol, can be identified on any future occasion, for it is only necessary to measure the crystal to be identified, deduce its complex-symbol from the form-development, and refer to the dictionary for a statement of the chemical composition.

Analytical and Crystallographic Details.

Following is a detailed summary of the results of chemical analysis and crystallographic measurement of the various substances prepared. Although measured angles only are reproduced in this paper (the angles which served as a basis for calculation being marked with an asterisk), it may be mentioned that the correctness of the various indices was checked by the logarithmic computation of the angular values demanded by the law of simple, rational indices, and that these computed angles were in every case satisfactorily close to the measured angles. The omission of these computed angles results in a great saving of space and does not seem to us to involve the loss of anything essential to the future usefulness of the crystallographic descriptions.

Tetramethylammonium Mercuri-iodide, Me_4NHgI_3.—M. p. above 200° (Found: Hg = 30·43. Calc.: Hg = 30·53 per cent.). Orthorhombic, $a:b:c = 0{\cdot}5777:1:0{\cdot}5199$. Forms: $b\{010\}$, $a\{100\}$, $m\{110\}$, $n\{120\}$, $c\{001\}$, $e\{101\}$, $p\{111\}$, $t\{121\}$. Two distinct habits were observed on crystals from acetone. The more usual habit is shown in Fig. 1. The second habit is bipyramidal and tabular parallel to $b\{010\}$. Following are the mean angular values obtained from five crystals:

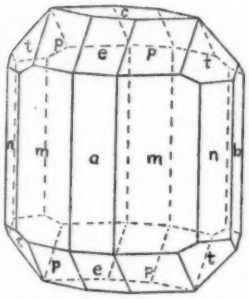
	$b\{010\}$.	$a\{100\}$.	$m\{110\}$.	$n\{120\}$.	$e\{101\}$.	$p\{111\}$.	$t\{121\}$.
Azimuth (ϕ)	0° 0′	90° 4′	*59°59′	40°50′	89°53′	59°59′	40°54′
Polar distance (ρ)	89°59′	89°59′	90° 0′	90° 2′	*41°59′	46° 3′	53°57′

Cleavages: $a\{100\}$, fair; $c\{001\}$, imperfect. Optic axial plane, $a\{100\}$; acute bisectrix, perpendicular to $\{001\}$; wide axial angle; birefringence, strong; dispersion $\rho > v$.

Trans.: 100/001/010. Complex-symbol, $(4d)69(+3)$.

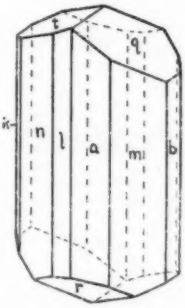
Methyltriethylammonium Mercuri-iodide, $MeEt_3NHgI_3$.—M. p. 104° (Found: Hg = 28·67. $C_7H_{18}NI,HgI_2$ requires Hg = 28·73 per cent.). Anorthic, $a:b:c = 1{\cdot}1202:1:0{\cdot}5578$; $\alpha = 102°55'$, $\beta = 93°56'$, $\gamma = 108°25'$. Forms: $b\{010\}$, $a\{100\}$, $m\{110\}$, $n\{1\bar{1}0\}$, $k\{1\bar{2}0\}$, $l\{2\bar{1}0\}$, $q\{011\}$, $t\{0\bar{1}1\}$, $r\{\bar{1}01\}$. The common habit is

Fig. 1.



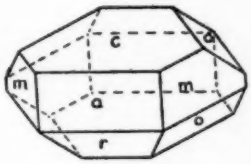
Tetramethylammonium mercuri-iodide.

Fig. 2.



Methyltriethylammonium mercuri-iodide.

Fig. 3.



Tetraethylammonium mercuri-iodide.

slender prismatic, as shown in Fig. 2. Following are the mean angular values obtained from nine crystals:

	$b\{010\}$.	$a\{100\}$.	$m\{110\}$.	$n\{1\bar{1}0\}$.	$k\{1\bar{2}0\}$.
Azimuth (ϕ)	0° 0′	*70° 5′	*32°18′	130°40′	154°17′
Polar distance (ρ) ...	90° 0′	90° 0′	90° 0′	90° 0′	90° 0′

	$l\{2\bar{1}0\}$.	$q\{011\}$.	$t\{0\bar{1}1\}$.	$r\{\bar{1}01\}$.
Azimuth (ϕ)	104° 5′	*4°29′	168°32′	281°43′
Polar distance (ρ) ...	90° 0′	*41°21′	*19° 3′	23°41′

Cleavages: $m\{110\}$ and $n\{1\bar{1}0\}$, good. Optics: All the prism faces give oblique extinction.

Trans.: $\bar{1}02/102/120$. Complex-symbol, $(4d; \pm 21)62(0; 0, ?)$.

Tetraethylammonium Mercuri-iodide, Et_4NHgI_3.—M. p. 110° (Found: Hg = 27·95. Calc.: Hg = 28·13 per cent.). Monoclinic, $a:b:c = 1{\cdot}4826:1:0{\cdot}8192$; $\beta = 107°55'$. Forms. $a\{100\}$, $m\{110\}$, $c\{001\}$, $r\{\bar{2}01$, $o\{\bar{1}11\}$. The common habit is stout prismatic, as shown in Fig. 3. Following are the mean angular values obtained from five crystals:

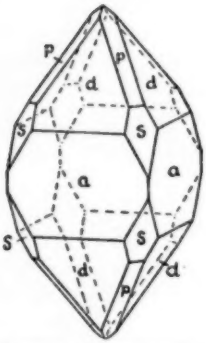
	$a\{100\}$.	$m\{110\}$.	$c\{001\}$.	$r\{\bar{2}01\}$.	$o\{111\}$.
Azimuth (ϕ)	90° 0′	*35°20′	89°46′	269°58′	*342°34′
Polar distance (ρ) ...	90° 0′	90° 0′	17°54′	39°56′	*40°39′

Cleavages: $a\{100\}$, perfect; $c\{001\}$, imperfect. Optic axial plane, $b(010)$. An optic axis emerges nearly perpendicular to $c(001)$.

Trans.: $011/01\bar{1}/101$. Complex-symbol, $(4d;\ -14\frac{1}{2})55(-6\frac{1}{2})$.

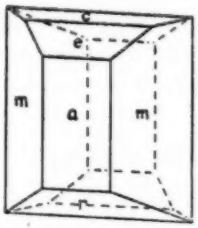
Tetraethylammonium Mercuri-iodide, $2Et_4NI,3HgI_2$.—M. p. 154° (Found: Hg = 31·94. Calc.: Hg = 31·98 per cent.). Tetragonal, $c:a = 0{\cdot}8186:1$. Forms: $a\{100\}$, $m\{110\}$, $e\{101\}$, $d\{201\}$, $p\{111\}$, $s\{221\}$. The common habit of the crystals is shown in Fig. 4. Following are the mean angular values obtained from four crystals:

FIG. 4.



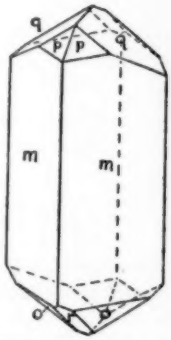
Tetraethylammonium mercuri-iodide.

FIG. 5.



Triethylpropylammonium mercuri-iodide.

FIG. 6.



Methyltripropyl-ammonium mercuri-iodide.

	$a\{100\}$.	$m\{110\}$.	$e\{101\}$.	$d\{201\}$.	$p\{111\}$.	$s\{221\}$.
Azimuth (ϕ)	0° 0′	45° 0′	0° 3′	0° 3′	45° 3′	45° 2′
Polar distance (ρ)	90° 0′	90° 8′	39°13′	*58°35′	49° 9′	66°35′

Cleavage: $a\{100\}$, good. Double refraction, very strong; positive. Complex-symbol, $(4h)49°9'$.

Triethyl-α-propylammonium Mercuri-iodide, $Et_3Pr^{\alpha}NHgI_3$.—M. p. 85° (Found: Hg = 27·33. $C_9H_{22}NI,HgI_2$ requires Hg = 27·58 per cent.). Monoclinic, $a:b:c = 1{\cdot}1350:1:0{\cdot}7359$, $\beta = 97°11'$. Forms: $a\{100\}$, $m\{110\}$, $c\{001\}$, $e\{101\}$, $r\{\bar{1}01\}$, $p\{111\}$. Two habits were observed, one of which is shown in Fig. 5. The second habit shows the pyramid $p\{111\}$, and $a\{100\}$ is much narrower. Following are the mean angular values obtained from six crystals:

	$a\{100\}$.	$m\{110\}$.	$c\{001\}$.	$e\{101\}$.	$r\{\bar{1}01\}$.	$p\{111\}$.
Azimuth (ϕ)	90° 0′	*41°36′	89°58′	89°59′	270° 4′	46°39′
Polar distance (ρ)	90° 0′	90° 0′	7° 5′	*37°51′	27°58′	*46°59′

Cleavage: $m\{110\}$, perfect. Optic axial plane, $b(010)$. An optic axis is visible through $a\{100\}$ on the extreme edge of the field.

Trans.: $\bar{1}10/\bar{1}\bar{1}0/002$. Complex-symbol, $(3h\,;+2)58(0)$.

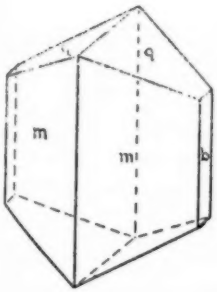
Methyltri-α-propylammonium Mercuri-iodide, $MePr^{\alpha}_3NHgI_3$.—M. p. 123° (Found: Hg = 26·55. $C_{10}H_{24}NI,HgI_2$ requires Hg = 27·06 per cent.). Monoclinic, $a:b:c = 1·0749:1:0·6542$; $\beta = 93°22'$. Forms: $m\{110\}$, $q\{011\}$, $r\{\bar{1}01\}$, $p\{111\}$, $o\{\bar{1}11\}$. Two distinct habits were observed, one of which is shown by Fig. 6. The second habit is stout prismatic with large pyramidal faces. Following are the mean angular values obtained from five crystals:

	$m\{110\}$.	$q\{011\}$.	$r\{\bar{1}01\}$.	$p\{111\}$.	$o\{\bar{1}11\}$.
Azimuth (ϕ)	*42°59′	4°59′	269°53′	*45°37′	319°50′
Polar distance (ρ) ...	90° 1′	33°24′	28°56′	*43° 5′	40°26′

Cleavages: $q\{011\}$, fair; $m\{110\}$, imperfect. Optic axial plane, $b(010)$, and an optic axis is visible through $a(100)$ on the edge of the field.

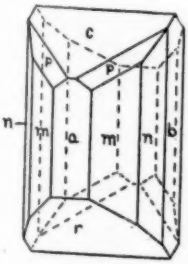
Trans.: $\bar{1}10/\bar{1}\bar{1}0/002$. Complex-symbol, $(4o\,;+3\frac{1}{2})50(-2)$.

FIG. 7.



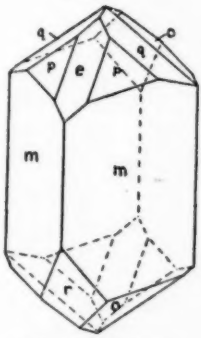
Ethyltripropylammonium mercuri-iodide.

FIG. 8.



Tetrapropylammonium mercuri-iodide.

FIG. 9.



Phenyltrimethyl-ammonium mercuri-iodide.

Ethyltri-α-propylammonium Mercuri-iodide, $EtPr^{\alpha}_3NHgI_3$.—M. p. 135° (Found: Hg = 26·43. $C_{11}H_{26}NI,HgI_2$ requires Hg = 26·56 per cent.). Orthorhombic, $a:b:c = 0·6890:1:0·5106$. Forms: $b\{010\}$, $m\{110\}$, $q\{011\}$. The common habit is shown in Fig. 7. A second habit was observed much shortened along the vertical axis. Following are the mean angular values obtained from six crystals:

	$b\{010\}$.	$m\{110\}$.	$q\{011\}$.
Azimuth (ϕ)	0° 0′	*55°26′	0° 0′
Polar distance (ρ) ...	89°58′	90° 0′	*27° 3′

Cleavages: $q\{011\}$, perfect; $c\{001\}$, imperfect. Optic axial plane, $a(100)$, and the c-axis is the negative acute bisectrix.

Trans.: $100/01\bar{1}/00\bar{2}$ Complex-symbol, $(6)37\frac{1}{2}(+3)$.

Tetra-α-propylammonium Mercuri-iodide, $Pr^{\alpha}_4NHgI_3$.—M. p. 178° (Found: Hg = 25·75. $C_{12}H_{28}NI,HgI_2$ requires Hg = 26·07 per cent.). Monoclinic, $a : b : c = 1{\cdot}4965 : 1 : 0{\cdot}7328$; $\beta = 113°16'$. Forms: $b\{010\}$, $a\{100\}$, $m\{110\}$, $n\{120\}$, $c\{001\}$, $r\{\bar{2}01\}$, $p\{111\}$. The habit is prismatic, as shown in Fig. 8. Following are the mean angular values obtained from five crystals:

	$b\{010\}$.	$a\{100\}$.	$m\{110\}$.	$n\{120\}$.	$c\{001\}$.
Azimuth (ϕ)	0° 0′	90° 0′	*36° 2′	20° 1′	89°58′
Polar distance (ρ) ...	90° 0′	90° 2′	90° 2′	90° 0′	*23°16′

	$r\{\bar{2}01\}$.	$p\{111\}$.
Azimuth (ϕ)	270° 0′	52°45′
Polar distance (ρ) ...	32°19′	*50°26′

Cleavages: $m\{110\}$ and $r\{\bar{2}01\}$, good. Optic axial plane, $b(010)$. An optic axis emerges nearly perpendicular to $r\{\bar{2}01\}$ and the acute negative bisectrix nearly coincides with the c-axis. Dispersion, moderate, $\rho > v$.

Trans.: $0\bar{1}1/011/\bar{1}0\bar{1}$. Complex-symbol, $(3d; -14)50(+1\frac{1}{2})$.

Phenyltrimethylammonium Mercuri-iodide, $PhMe_3NHgI_3$.—M. p. 135° (Found: Hg = 27·80. $C_9H_{14}NI,HgI_2$ requires Hg = 27·89 per cent.). Monoclinic, $a : b : c = 1{\cdot}2400 : 1 : 0{\cdot}6783$; $\beta = 104°54'$. Forms: $a\{100\}$, $m\{110\}$, $n\{210\}$, $q\{011\}$, $e\{101\}$, $r\{\bar{3}01\}$, $p\{111\}$, $o\{\bar{1}11\}$. The habit is prismatic, as shown in Fig. 9. Following are the mean angular values as obtained from five crystals:

	$a\{100\}$.	$m\{110\}$.	$n\{210\}$.	$q\{011\}$.	$e\{101\}$.
Azimuth (ϕ)	90° 0′	*39°51′	59° 6′	21°28′	90° 0′
Polar distance (ρ) ...	90° 1′	90° 0′	90° 0′	36° 6′	*39°46′

	$r\{\bar{3}01\}$.	$p\{111\}$.	$o\{\bar{1}11\}$.
Azimuth (ϕ)	269°59′	50°54′	336° 4′
Polar distance (ρ) ...	55° 7′	*47° 2′	36°34′

Cleavage: $a\{100\}$, good. Optic axial plane, $b(010)$. Through $a\{100\}$ an optic axis is visible on the edge of the field.

Trans.: $\bar{1}10/\bar{1}\bar{1}0/002$. Complex-symbol, $(4o; +15)48\frac{1}{2}(-5)$.

Phenyldimethylethylammonium Mercuri-iodide, $PhMe_2EtNHgI_3$.—M. p. 95° (Found: Hg = 27·21. $C_{10}H_{16}NI,HgI_2$ requires Hg = 27·36 per cent.). Monoclinic, $a : b : c = 0{\cdot}7391 : 1 : 0{\cdot}6783$; $\beta = 94°6'$. The common habit is that of unmeasurable radiating needles. A few measurable crystals were obtained of the type shown in Fig. 10.

Forms: $m\{110\}$, $q\{011\}$, $e\{101\}$, $r\{\bar{1}01\}$, $c\{001\}$. Following are the mean angular values obtained from seven crystals (no trustworthy results were obtainable from the face c, which was always curved):

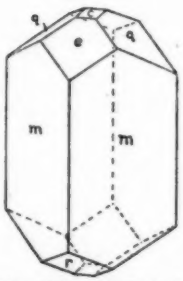
	$m\{110\}$.	$q\{011\}$.	$e\{101\}$.	$r\{\bar{1}01\}$.
Azimuth (ϕ)	*53°36′	*6° 2′	89°59′	270° 0′
Polar distance (ρ) ...	90° 1′	*34°18′	44°43′	40°22′

Cleavage: $c\{001\}$, perfect. Optic axial plane, $b(010)$. An optic axis is visible through $c\{001\}$ on the edge of the field. The dispersion of the optic axes is strong.

Trans.: $\bar{1}01/\bar{1}0\bar{1}/010$. Complex-symbol, $(4d;4)53(-2\frac{1}{2})$.

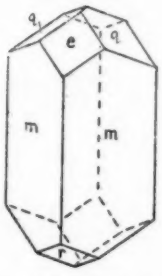
Phenyldimethyl-α-propylammonium Mercuri-iodide, $PhMe_2Pr^{\alpha}NHgI_3$. —M. p. 88° (Found: Hg = 26·54. $C_{11}H_{18}NI,HgI_2$ requires Hg = 26·84 per cent.). Monoclinic, $a:b:c = 0{\cdot}7775:1:0{\cdot}6711$; $\beta = 96°34'$. Forms: $m\{110\}$, $q\{011\}$, $e\{101\}$, $r\{\bar{1}01\}$. The common

FIG. 10.



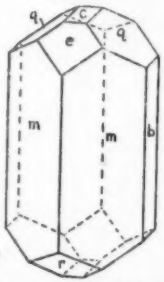
Phenyldimethylethyl-ammonium mercuri-iodide.

FIG. 11.



Phenyldimethylpropyl-ammonium mercuri-iodide.

FIG. 12.



Phenylmethyldiethyl-ammonium mercuri-iodide.

form is that of radiating needles. A few measurable crystals were obtained of the habit shown in Fig. 11, with prism faces much curved. Following are the mean angular values obtained from seven crystals:

	$m\{110\}$.	$q\{011\}$.	$e\{101\}$.	$r\{\bar{1}01\}$.
Azimuth (ϕ)	*53°19′	*9°44′	89°52′	269°57′
Polar distance (ρ) ...	90° 0′	*34°14′	44°44′	36°58′

Cleavage: $c\{001\}$, perfect. Optic axial plane perpendicular to $b(010)$. The acute negative bisectrix is nearly perpendicular to $c\{001\}$. Dispersion strong, $\rho > v$.

Trans.: $\bar{1}01/\bar{1}0\bar{1}/010$. Complex-symbol, $(4d;6\frac{1}{2})52\frac{1}{2}(-4)$.

Phenylmethyldiethylammonium Mercuri-iodide, $PhMeEt_2NHgI_3$. —M. p. 96° (Found: Hg = 26·63. $C_{11}H_{18}NI,HgI_2$ requires Hg =

26·84 per cent.). Monoclinic, $a:b:c=0{\cdot}7319:1:0{\cdot}6976$; $\beta=93°24'$. Forms: $b\{010\}$, $m\{110\}$, $n\{120\}$, $c\{001\}$, $q\{011\}$, $e\{101\}$, $r\{\bar{1}01\}$. The common habit is shown by Fig. 12. Following are the mean angular values obtained from five crystals:

	$b\{010\}$.	$m\{110\}$.	$n\{120\}$.	$c\{001\}$.	$q\{011\}$.
Azimuth (ϕ)	0° 0′	*53°51′	34°18′	89°54′	*4°52′
Polar distance (ρ) ...	90° 0′	90° 0′	90° 0′	3°25′	*34°57′

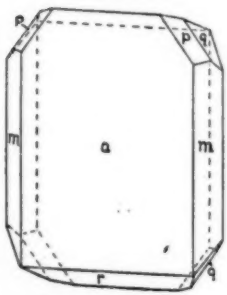
	$e\{101\}$.	$r\{\bar{1}01\}$.
Azimuth (ϕ)	90° 2′	269° 57′
Polar distance (ρ)	45°19′	41°42′

Cleavages: $c\{001\}$, perfect; $m\{110\}$, imperfect. Optic axial plane, $b(010)$. An optic axis is inclined at about 20° to $c\{001\}$. The double refraction is negative, with strong dispersion $\rho<v$.

Trans.: $\bar{1}01/101/010$. Complex-symbol, $(4d;\ 3)55(+2)$.

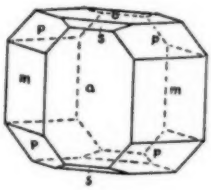
Phenyltriethylammonium Mercuri-iodide, $PhEt_3NHgI_3$.—M. p. 98° (Found: Hg=25·94. $C_{12}H_{20}NI,HgI_2$ requires Hg=26·35 per

FIG. 13.



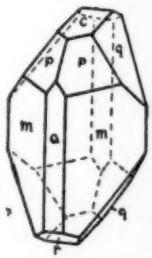
Phenyltriethylammonium mercuri-iodide (1 : 1).

FIG. 14.



Phenyltriethylammonium mercuri-iodide (2 : 1).

FIG. 15.



Phenyldiethylpropylammonium mercuri-iodide.

cent.). Monoclinic, $a:b:c=1{\cdot}1250:1:1{\cdot}3490$; $\beta=101°20'$. Forms: $a\{100\}$, $m\{110\}$, $r\{\bar{1}02\}$, $q\{011\}$, $p\{111\}$. The common habit is shown by Fig. 13. Following are the mean angular values obtained from five crystals:

	$a\{100\}$.	$m\{110\}$.	$r\{102\}$.	$q\{011\}$.	$p\{111\}$.
Azimuth (ϕ)	90° 0′	*42°12′	269°58′	8° 5′	*46°33′
Polar distance (ρ) ...	90° 0′	90° 1′	22°48′	53°39′	*62°59′

Cleavage: $a\{100\}$, perfect. Optic axial plane is $b(010)$. Inclined dispersion, strong.

Trans.: 001/100/010. Complex-symbol, $(4h;\ 9\frac{1}{2})46(-5\frac{1}{2})$.

Phenyltriethylammonium Mercuri-iodide, $2PhEt_3NI,HgI_2$.—M. p. 144° (Found: Hg=19·21. $(C_{12}H_{20}NI)_2HgI_2$ requires

Hg = 18·80 per cent.). Orthorhombic, $a:b:c = 0{\cdot}8642:1:1{\cdot}1605$. Forms: $a\{100\}$, $m\{110\}$, $c\{001\}$, $s\{104\}$, $p\{111\}$. The habit is shown by Fig. 14. Following are the mean angular values obtained from five crystals:

	$a\{100\}$.	$m\{110\}$.	$c\{001\}$.	$s\{104\}$.	$p\{\bar{1}11\}$.
Azimuth (ϕ)	90° 0′	*49°10′	—	89°58′	49°10′
Polar distance (ρ) ...	90° 0′	90° 0′	0° 0′	18°38′	*60°36′

Cleavage: $c\{001\}$, imperfect. Optic axial plane, $b(010)$; the acute bisectrix is perpendicular to $c\{001\}$. The optic axial angle is wide.

Trans.: 010/100/001. Complex-symbol, $(4d)60\frac{1}{2}(+4)$.

Phenyldiethyl-α-propylammonium Mercuri-iodide, $PhEt_2Pr^{\alpha}NHgI_3$.—M. p. 93° (Found: Hg = 26·33. $C_{13}H_{22}NI,HgI_2$ requires Hg = 25·87 per cent.). Monoclinic, $a:b:c = 1{\cdot}1185:1:1{\cdot}3440$; $\beta = 100°57'$. Forms: $a\{100\}$, $m\{110\}$, $c\{001\}$, $q\{011\}$, $r\{\bar{1}02\}$, $p\{111\}$. The common habit is shown by Fig. 15. Another habit was observed tabular to $a\{100\}$. Following are the mean angular values obtained from five crystals:

	$a\{100\}$.	$m\{110\}$.	$c\{001\}$.	$q\{011\}$.	$r\{\bar{1}02\}$.	$p\{111\}$.
Azimuth (ϕ)	90° 0′	*42°19′	90° 4′	8°10′	270°15′	*46°31′
Polar distance (ρ)	90° 1′	90° 1′	11° 0′	53°43′	22°45′	*62°53′

Cleavages: $a\{100\}$, perfect; $m\{110\}$, imperfect. Optic axial plane perpendicular to $b(010)$. The positive acute bisectrix is visible through $a\{100\}$ on the edge of the field. Dispersion, strong, $\rho < v$.

Trans.: 001/100/010. Complex-symbol, $(4h;11)50(+6)$.

Phenylbenzyldimethylammonium Mercuri-iodide, $Ph(CH_2Ph)Me_2NHgI_3$.—M. p. 143° (Found: Hg = 24·74. $C_{15}H_{18}NI,HgI_2$ requires Hg = 25·22 per cent.). Monoclinic, $a:b:c = 0{\cdot}7386:1:0{\cdot}5105$, $\beta = 92°26'$. Forms: $b\{010\}$, $a\{100\}$, $m\{110\}$, $q\{011\}$, $r\{\bar{1}01\}$, $s\{121\}$, $v\{\bar{1}41\}$, $t\{321\}$. The common habit is shown in Fig. 16. Following are the mean angular values obtained from five crystals:

	$b\{010\}$.	$a\{100\}$.	$m\{110\}$.	$q\{011\}$.	$r\{\bar{1}01\}$.
Azimuth (ϕ)	0° 0′	89°59′	*53°34′	4°44′	270° 1′
Polar distance (ρ) ...	90° 0′	90° 0′	90° 0′	27° 7′	32°57′

	$s\{121\}$.	$v\{\bar{1}41\}$.	$t\{321\}$.
Azimuth (ϕ)	*35°43′	342°24′	296°41′
Polar distance (ρ) ..	51°31′	65° 1′	66°15′

Cleavage: $a\{100\}$, fair. Optic axial plane, $b(010)$.

Trans.: $0\bar{1}0/\bar{1}0\bar{1}/\bar{1}03$. Complex-symbol, $(4d;-7\frac{1}{2})69(+4)$.

Phenylbenzylmethylethylammonium Mercuri-iodide, $Ph(CH_2Ph)MeEtNHgI_3$.

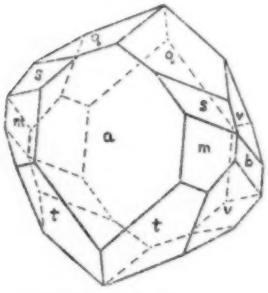
—M. p. 127° (Found: Hg = 24·68. $C_{16}H_{20}NI,HgI_2$ requires Hg = 24·78 per cent.). Monoclinic, $a:b:c = 0·9878:1:0·5797$, $\beta = 106°9'$. Forms: $b\{010\}$, $a\{100\}$, $m\{110\}$, $c\{001\}$, $q\{011\}$, $r\{\bar{2}01\}$. The habit is shown in Fig. 17. Following are the mean angular values obtained from seven crystals:

	$b\{010\}$.	$a\{100\}$.	$m\{110\}$.	$c\{001\}$.	$q\{011\}$.	$r\{\bar{2}01\}$.
Azimuth (ϕ)	0° 0′	90° 1′	*46°30′	90° 8′	26°37′	269°58′
Polar distance (ρ)	90° 0′	90° 0′	90° 0′	16° 9′	32°57′	42°51′

Cleavage: $m\{110\}$, good. Optic axial plane is $b(010)$. An optic axis is visible through $r\{\bar{2}01\}$. The dispersion is strong.

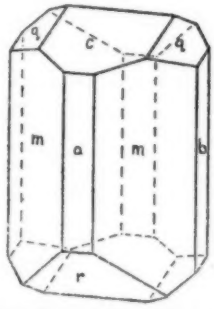
Trans.: 010/100/001. Complex-symbol, $(4h; -16)40(1\frac{1}{2})$.

FIG. 16.



Phenylbenzyldimethylammonium mercuri-iodide.

FIG. 17.



Phenylbenzylmethylethylammonium mercuri-iodide.

Phenylbenzyldiethylammonium Mercuri-iodide, $Ph(CH_2Ph)Et_2NHgI_3$.

—M. p. 138·5° (Found: Hg = 23·71. $C_{17}H_{22}NI,HgI_2$ requires Hg = 24·36 per cent.). Monoclinic, $a:b:c = 1·0301:1:0·6354$, $\beta = 108°7'$. Forms: $m\{110\}$, $c\{001\}$, $q\{011\}$, $r\{\bar{2}01\}$. The crystals are curved and distorted. The common habit is shown in Fig. 18. Following are the mean angular values obtained from seven crystals:

	$m\{110\}$.	$c\{001\}$.	$q\{011\}$.	$r\{\bar{2}01\}$.
Azimuth (ϕ)	*45°36′	90° 0′	*27°14′	270° 0′
Polar distance (ρ) ...	90° 0°	18°25′	35°33′	43°49′

Cleavages: $c\{001\}$, imperfect; $r\{\bar{2}01\}$, perfect. Optic axial plane, $b(010)$, and there is an optic axis visible through $r\{\bar{2}01\}$ on the edge of the field. There is strong dispersion.

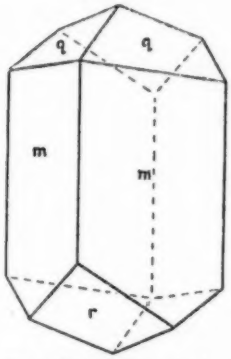
Trans.: 010/100/001. Complex-symbol, $(4h; -18)42(\frac{1}{2})$.

Phenylbenzylmethyl-α-propylammonium Mercuri-iodide, $Ph(CH_2Ph)Et_2NHgI_3$.

—M. p. 134° (Found: Hg = 24·34. $C_{17}H_{22}NI,HgI_2$ requires Hg = 24·36 per cent.). Monoclinic, $a:b:c = 1·1060:1:0·7766$, $\beta = 102°55'$. Forms: $a\{100\}$, $m\{110\}$, $c\{001\}$, $r\{\bar{1}01\}$, $s\{221\}$, $x\{\bar{2}21\}$. The common habit is shown by Fig. 19. Following are the mean angular values obtained from seven crystals:

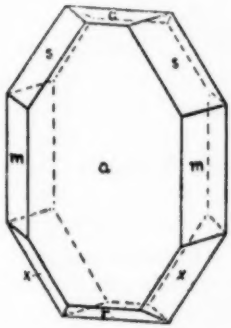
	$a\{100\}$.	$m\{110\}$.	$c\{001\}$.	$r\{\bar{1}01\}$.	$s\{221\}$.	$x\{\bar{2}21\}$
Azimuth (ϕ)	90° 0′	*42°51′	89°52′	270° 0′	*47° 4′	321°45′
Polar distance (ρ)	90° 0′	90° 0′	12°36′	26°45′	66°19′	63° 1′

FIG. 18.



Phenylbenzyldiethylammonium mercuri-iodide.

FIG. 19.



Phenylbenzylmethylpropyl-ammonium mercuri-iodide.

Cleavage: $a\{100\}$. The optic axial plane is perpendicular to the plane of symmetry, and an optic axis is visible through $m\{110\}$. Trans.: 100/010/002. Complex-symbol, $(4d; +13)64\frac{1}{2}(+2)$.

Our thanks are due to the Research Fund Committee of the Chemical Society and to the Scientific and Industrial Research Department for grants in aid of this work, and also to Professor H. L. Bowman, Mr. J. E. Marsh, and Professor W. H. Perkin for much help and advice.

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CXLII.—*Studies on Hypophosphorous Acid. Part II. Its Reaction with Iodine.*

By Alec Duncan Mitchell.

In estimating hypophosphorous acid by means of mercuric chloride according to the method given by Treadwell ("Quantitative Analysis," p. 289), it was found that the oxidation proceeded readily to phosphorous acid, but relatively slowly to phosphoric acid. It was therefore decided to investigate the progress of the reaction, and certain facts were noted in the first stage—the oxidation to phosphorous acid—which are, briefly:

(1) The concentration of mercuric chloride appeared to have no influence on the reaction velocity except when very dilute.

(2) The reaction was accelerated by the addition of hydrochloric acid.

(3) It was therefore auto-catalytic, owing to the hydrochloric acid produced.

(4) The initial velocity was approximately proportional to the product of the concentrations of the hydrogen ions and the hypophosphorous acid.

From these facts, it was concluded that the oxidation to phosphorous acid involved two successive reactions: the first, of measurable velocity, in which the mercuric chloride took no part, and the second, of relatively great velocity, in which the mercuric chloride functioned. No conventional hypothesis appeared adequately to explain these facts.

In order to investigate certain points more fully, an analogous reaction was sought in which the analytical method used would be of greater applicability. The reaction with iodine was found to be accurately comparable, and is here described. That with mercuric chloride will be communicated later, but it may be mentioned that comparative experiments with iodine and mercuric chloride, respectively, showed that the measurable velocity was identical in the two cases, thus lending additional support to the view that only hypophosphorous acid functions in the slower reaction.

Steele (T., 1907, **91**, 1641) had already investigated the reaction with iodine, and obtained the same general results as above. For the reaction $H_3PO_2 + I_2 + H_2O = H_3PO_3 + 2HI$ he offered the following explanation: the slow stage is represented by

$$(1)\quad H_2PO_3' + H_2O \longrightarrow HPO_3'' + 3H^{\cdot} + 2\ominus,$$

which proceeds, liberating free ionic charges, if there is also present a

substance capable of utilising them as rapidly as they are formed: (2) $I_2+2\ominus=2I'$. He points out that several hypothetical schemes may be substituted for (1) in order to account for the production of free electrons, but that intermediate compounds containing iodine cannot be formed in this stage. Any equilibrium between hypophosphorous acid and an "active" form would not agree with the facts if it be assumed that equilibrium is instantaneously restored; but it is now shown that, if equilibrium is restored at a finite rate, the existence of an intermediate "active" form adequately agrees with the facts and renders unnecessary the above unconventional hypothesis.

The reaction has now been studied under more diverse conditions, and certain new aspects have been investigated.

Steele ignored two factors, which are here shown to have an important bearing on the problem:

(1) The depression by mineral acids of the ionisation of hypophosphorous acid, which he regarded as "probably slight." Taking this into account by utilising data obtained in the author's paper on the subject (this vol., p. 957), it is shown clearly that the effect is considerable, and that hypophosphorous acid functions as undissociated molecules. Steele obtained higher constants in stronger acid solutions than in weaker, but, instead of attributing this to the increased proportion of molecules, he ascribed it to the fact that he was using more dilute hypophosphorous acid solutions, the behaviour of which he thought anomalous, and suggested the idea that its ions were the active part of the acid.

(2) The part played by the iodine, which is apparently negligible over small ranges at moderate concentration, but becomes relatively great as the concentration decreases. Steele suggested that it played no part in the reaction until about nine-tenths of it had been used up, but that it then took part in an apparently bimolecular reaction. This is now shown to be erroneous. Also, he was led to ascribe certain discrepancies to the above-mentioned anomalous behaviour of hypophosphorous acid in dilute solution, but these are now shown to be regularised when the function of the iodine is considered.

From the data obtained from about thirty experiments now described, actual rates of decrease (ds/dt) of hypophosphorous acid were calculated at the beginning, middle, and end of each experiment, and when these were divided by the concentrations, at time t, of hypophosphorous acid, l_t, and hydrogen ions, h_t, and by the proportion of undissociated hypophosphorous acid molecules, $1-\alpha_t$, ninety values were obtained for the expression $(ds/dt)/h_t l_t(1-\alpha_t)$ which were almost constant when the corresponding concentrations

of iodine exceeded $N/50$, but which decreased more and more rapidly with decreasing concentrations of iodine. This behaviour was ultimately found to be represented by the formula

$$[1+rh_t/a_t](ds/dt)=kh_tl_t(1-a_t),$$

where a_t represents the concentration of the iodine molecules and r and k are constants.

It will be noticed that this equation takes the form

$$ds/dt=kl_t(1-a_t)h_ta_t/(a_t+rh_t)$$

which the reaction would give if it were simply bimolecular between hypophosphorous acid molecules and iodine, being accelerated by hydrogen ions and retarded by a function, a_t+rh_t, of the iodine. Meyerhoffer (*Zeitsch. physikal. Chem.*, 1888, **2**, 585) found that iodine had a retarding effect, proportional to its concentration plus a constant, on the reaction $HBrO_3+6HI=HBr+3H_2O+3I_2$; but the slightly modified form mentioned above has not been regarded as a valid explanation of the present reaction, since it is difficult to understand why iodine should exert a retarding effect when its concentration is zero, and its acceptance would imply that the hydrogen ions had simultaneously both accelerating and inhibiting effects.

The following hypothesis is found to require the same mathematical expression and to fulfil all the other requirements previously postulated. Hypophosphorous acid molecules are originally in equilibrium with a very small quantity, y, of an "active" form, say H_5PO_3, in which the action of the hydrogen ions is to accelerate re-establishment of equilibrium:

$$H_3PO_2+H_2O \rightleftharpoons H_5PO_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and the iodine, reacting, as shown later, as the I_3' ion, takes part:

$$H_5PO_3+I_3' \longrightarrow H_3PO_3+2H^{\cdot}+3I' \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The rate of formation of phosphorous acid, according to (4), will be:

$$ds/dt = k_2y_ta_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

k_2 being a very large reaction velocity-constant. The equilibrium in (3) is

$$kl_t(1-a_t)h_t=k_1y_th_t \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

k and k_1 being the reaction velocity-constants in the two directions, k_1 being large, but not infinite, and the amount, y_t, being so small as not appreciably to affect the amount of hypophosphorous acid.

Then the rate of increase in y, owing to the tendency to restore equilibrium, is $kl_t(1-a_t)h_t-k_1y_th_t$, from (6), and its rate of decrease is ds/dt; hence

$$dy/dt=kl_t(1-a_t)h_t-k_1y_th_t-ds/dt \quad . \quad . \quad . \quad . \quad (7)$$

Eliminating y_t from (5) and (7), we have

$$(d^2s/dt^2)/k_2 + (ds/dt)^2/k_2a_t + [a_t + k_1h_t/k_2]ds/dt = ka_tl_t(1-a_t)h_t \quad (8)$$

This expression can be simplified for most reactions, as follows. Since k_2 is very large and k_1 moderately large compared with k, and d^2s/dt^2 and $(ds/dt)^2$ are of a lower order of magnitude than the other terms, and, moreover, are of opposite sign (except in certain cases), the first two terms may be neglected as a first approximation, and one has

$$[a_t + k_1h_t/k_2]ds/dt = ka_tl_t(1-a_t)h_t$$

or

$$[1 + k_1h_t/k_2a_t]ds/dt = kl_t(1-a_t)h_t \quad . \quad . \quad . \quad . \quad (9)$$

which is identical with the formula obtained experimentally when the constant k_1/k_2 is replaced by the constant r. As the best value of r is found to be 0·012, this explains why the iodine appears not to function until it becomes dilute, when a_t is small.

Now, $l_t = l - s$, $a_t = a - s$, and $h_t = h + ms$, since h_t is found to be a linear function of s. If, therefore, a_t is a simple function of s, the expression can be integrated. In some cases it is a linear function, so that $a_t = a - ns$. Letters without suffixes denote initial values, and m and n are constants for any particular experiment. The expression simplifies to

$$k\,.\,dt = ds[1/(l-s)(h+ms)(1-a+ns) + r/(l-s)(a-s)(1-a+ns)] \quad (9a)$$

and one obtains, on integration,

$$kt = \frac{1}{(1-a+nl)(h+ml)[m(1-a)-hn]}\left[\{m(1-a)-hn\}\log\frac{l}{l-s} - n(h+ml)\log\frac{1-a+ns}{1-a} + m(1-a+ln)\log\frac{h+ms}{h}\right] +$$

$$\frac{0{\cdot}012}{(l-a)(1-a+ln)(1-a+na)}\left[(1-a+ln)\log\frac{a}{a-s} - (1-a+na)\log\frac{l}{l-s} + n(l-a)\log\frac{1-a+ns}{1-a}\right] \quad . \quad . \quad (10)$$

In cases where a_t is not sufficiently nearly a linear function of s, it is better to put $n=0$, regarding a as constant, and subsequently to employ the average value of $(1-a)$ for the period concerned in obtaining the value of the constant. Thus one has

$$(1-a)kt = \left[\log l - l - s + \log\frac{h+ms}{h}\right]\Big/(h+ml) + 0{\cdot}012\left[\log\frac{a}{a-s} - \log\frac{l}{l-s}\right]\Big/(l-a) \quad . \quad . \quad (11)$$

The exceptional cases mentioned when simplifying (8) to (9) are those in which the initial hydrogen-ion concentration is relatively

small and the reaction velocity increases at first to a maximum, so that d^2s/dt^2 is not negative until that maximum is passed. These cases give results in fair agreement with the others when formula (11) is used, so that even when both the neglected terms in (8) are positive, their combined effect is very slight.

It is interesting to note that if hydrogen ions actually took part in the reaction (3) in one direction only, and were not merely catalytic, h_t would disappear from the second term on the left of equation (9), and the theory would require results not consistent with practice.

In the calculations, it is assumed that α for the hypophosphorous acid depends only on the initial amount present and on the concentration of the hydrogen ions, and is not affected by the replacement of hypophosphorous acid by phosphorous acid. This assumption is justified, because the ionising powers of the two acids are very similar, and the total of the two acids remains unchanged, so that, according to the "total ion" hypothesis (Arrhenius, *Zeitsch. physikal. Chem.*, 1888, **2**, 285; 1899, **31**, 218; Bray and Hunt, *J. Amer. Chem. Soc.*, 1911, **33**, 781; and Mitchell, this vol., p. 957), for any definite hydrogen-ion concentration there is a definite value of α for each initial concentration of hypophosphorous acid. Also it does not appear that the undissociated molecules of the mineral acids have any appreciable catalytic influence in the concentrations used.

In several experiments (Nos. I, II, and V), possible oxidation to phosphoric acid was checked alkalimetrically (see p. 1332) and found to be negligible. It has, indeed, been shown to be inhibited in an acid medium (Boyer and Bauzil, *J. Pharm. Chim.*, 1918, [vii], **18**, 321), and Federlin (*Zeitsch. physikal. Chem.*, 1902, **41**, 565) could only obtain measurable velocities for the reaction between phosphorous acid and iodine by using concentrated solutions.

In one phase of this work, in order to obtain small yet constant concentrations of hydrogen ions, a "regulator" solution was used, consisting of equimolecular proportions of phosphoric acid and potassium dihydrogen phosphate, so that in the reaction-mixture each was present in molar concentration. Since the concentration of hydrogen ions was constant, the degree of ionisation of hypophosphorous acid was also constant, and, for these experiments, (9) becomes

$$(1+r'/a_t)ds/dt = k'l_t \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where r' and k' are constants, r' being assigned the value 2·0 as giving most consistent results. Attempts to relate r' to rh and k' to $k(1-\alpha)h$, which they replace, are complicated by lack of

sufficient data for such concentrated solutions, but h is of the order $N/50$ and $(1-\alpha)$ about 0·4, so that it is concluded that both k' and r' are several times greater than would be expected.

Owing to the form of equations (11) and (12), in many cases they gave extremely concordant values of a constant based on the equation $ds/dt = k''l_t\sqrt{a_t}$, which was found not to hold when applied to iodine concentrations of a different order. In experiments XI, XX, and XXV this constant is given, as well as k or k', as an interesting example of the danger of relying on what happens to be merely a mathematical coincidence.

The integrated form of (12) is

$$k't = \log\frac{l}{l-s} + \frac{2\cdot0}{l-a}\left(\log\frac{a}{a-s} - \log\frac{l}{l-s}\right) \quad . \quad . \quad (13)$$

The I_3' *Ion.*—Considering the equilibrium $I_3' \rightleftharpoons I_2 + I'$ investigated by Jakowkin (*Zeitsch. physikal. Chem.*, 1896, **20**, 19), it can be shown that, for any stage of the reaction,

$$[I_2] = K(a-s)/(p+s-a)$$

to a close degree of approximation, where p is the molar concentration of the potassium iodide (assumed completely ionised), and that $[I_3'] = (a-s)[1-K/(p+s-a)]$, since p increases by $2s$ and a decreases by s, when s molecules of iodine have been changed to iodide ions. At the beginning of an experiment, when s is zero, $[I_2] = Ka/(p-a)$, and is therefore independent of the concentration. It was at first thought that this would account for the peculiar behaviour of the iodine in apparently not affecting the velocity of the reaction; but $[I_2]$ decreases more rapidly than $a-s$ with increase of s, so that, if the iodine reacted as such, its apparent active mass should fall off more rapidly than $a-s$, whereas actually it changes far less rapidly. Moreover, a comparison was made in experiments XII and I which were identical, except that in XII potassium iodide was added, so that p was equal to $9\cdot78a$, whereas in I it was $3\cdot76a$; if molecular iodine were the active factor, the initial reaction velocities should be in the ratio 2·76 to 8·78, whereas they were almost identical. Experiments XXV and XXVI also illustrate this in presence of the "regulator" solution. The iodine therefore does not react as molecules.

Thus it is the I_3' ion which functions, and, using the constant 0·00135 given by Jakowkin for the equilibrium, it is found that this ion constitutes 99 per cent. of the available iodine in $N/10$-solutions, but is less in weaker solutions, being only about 65 per cent. in $N/400$-solutions at the beginning of reactions, and increasing somewhat as the reaction proceeds. This change in the relative concentration of the I_3' ion has been ignored throughout, as the

correction involved only affects the smaller term, and is, moreover, less at the end of a reaction than at the beginning, since the increase of iodide ions outweighs the effect of dilution, and thus increases the proportion of I_3' ions. It would unnecessarily complicate equations, which are evidently sufficiently accurate to demonstrate the validity of the hypothesis.

In conclusion, it may be said that, whatever the nature of the supposed "active" form of hypophosphorous acid, its existence could probably not be detected by chemical means, and, as the indications are that it is less than 1 per cent. of (and in constant proportion to) the acid molecules, its detection by physical means would be difficult. It is also possible that another hypothesis could be found which would require similar mathematical expression, but, if so, it is certainly more complicated than that developed here.

Experimental.

The reactions were carried out in stoppered brown glass bottles in a thermostat at 25±0·05°. The iodine solution and hydrochloric acid or "regulator" solutions, when used, were made up to 400 c.c., and when they had acquired the temperature of the thermostat, 1·013, 2·000, or 4·000 c.c. of a concentrated solution of hypophosphorous acid were added from standardised pipettes. At definite times, quantities were withdrawn and run into a large volume of water containing the volume of standard sodium thiosulphate solution estimated to be necessary, and the final adjustment made at once. Check experiments showed that the hypophosphorous acid did not affect the titrations.

The stock iodine solution was accurately decinormal. As it was subsequently required to know the potassium iodide content of this solution, it was found to be 31·2 grams per litre (or 3·76 molecules per molecule of iodine) by an adaptation of the method with potassium iodate described by Sutton ("Volumetric Analysis," p. 133).

The stock hypophosphorous acid solution was a chemically pure article of commerce (D 1·14) which showed no impurities other than a little phosphorous acid. Its composition was checked by two methods: 25 c.c. of a one-tenth solution gave 1·5124 grams of $Mg_2P_2O_7$, therefore $H_3PO_2 + H_3PO_3 = 5·45$ moles. per litre; 20 c.c. of one-fiftieth solution required 21·80 c.c. of $N/10$-NaOH with methyl-orange, and 22·60 c.c. with phenolphthalein. Since hypophosphorous acid is monobasic to both indicators and phosphorous acid is monobasic to the former and dibasic to the latter, the former is 5·25 molar and the latter is 0·20 molar, thus giving

a total identical with the gravimetric value. For obtaining the value of l, the solution was regarded as $5{\cdot}25N$, and the values of the hydrogen ions were based on a normality of 5·45, since the second hydrogen ion of phosphorous acid can be ignored.

Calculation of Results.—The degrees of dissociation of hydrochloric acid are taken from the results of Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781), and the hydriodic acid is reckoned as hydrochloric acid for this purpose. The degree of dissociation of the hypophosphorous acid in the presence of the mineral acids is obtained by methods based on the author's recent communication on the subject (this vol., p. 957). From table I given therein, a curve is constructed showing the relation between α and the concentration of hydrogen ions, α/v, when no extraneous acid is present. From this it is possible to obtain a series of curves, one for each value of l, showing the relation between α and the concentration of extraneous hydrogen ions ($H^{\cdot}_x$), as follows: for a definite concentration of hypophosphorous acid, l, the value of α when $H^{\cdot}_x$ is zero can be obtained at once. A slightly lower value, α_1, is then selected, and the concentration of hydrogen ions in equilibrium with the acid alone at that degree of ionisation is found from the first curve; this must also be the concentration of hydrogen ions in the equilibrium if foreign acid is present, as shown in the paper quoted; from this is therefore deducted $l\alpha_1$, due to the hypophosphorous acid itself, and the remainder is $H^{\cdot}_x$. A series of corresponding values of α and $H^{\cdot}_x$ is obtained in this way for each value of l, and from the resulting curve the value of α can be obtained for a known $H^{\cdot}_x$. This method is simpler and of wider applicability than solving the equation developed in the former communication.

In order to avoid small decimals, all concentrations are multiplied by 200, and the value of k should therefore be multiplied by 200 in order to give absolute units. Time, t, is in minutes; $a-s$ shows the iodine concentration in molecules; s shows the number of moles. reduced; $l-s$ the hypophosphorous acid remaining. The column HI shows the original hydrochloric acid (when used) plus $2s$, the hydriodic acid formed. $H^{\cdot}_{HI}$ are the corresponding hydrogen-ion concentrations of the mineral acids, the degree of ionisation (not recorded) being assumed to be unaffected by the presence of the weaker acids. α gives the degree of dissociation of the hypophosphorous and phosphorous acid, and under $H^{\cdot}_P$ is recorded $l\alpha$, the hydrogen ions derived from them, the slight correction necessary for the phosphorous acid initially present having been made throughout. Then follow the total hydrogen-ion concentration, h, and $1-\alpha_M$, the mean value of $1-\alpha$ for the period

(or $1-\alpha_H$, the value at the middle of the period), for which the constant k is calculated.

Formula (11) is used except where otherwise stated, and in any one experiment the deviations of k from the mean rarely exceed 3 per cent.

The six following experiments were without original hydrochloric acid.

Experiment I.

t.	$a-s$.	s.	$l-s$.	HI.	H'_{HI}.	α.	H'_P.	h.	$1-\alpha_M$.	$k\times10^5$
0	4·99	—	10·52	—	—	0·645	7·10	7·10	—	—
5	4·82	0·17	10·35	0·34	0·34	0·640	6·99	7·33	0·355	118
20	4·34	0·65	9·86	1·31	1·28	0·625	6·77	8·05	0·365	114
50	3·29	1·70	8·82	3·40	3·27	0·590	6·44	9·71	0·382	112
80	1·96	3·03	7·48	6·07	5·77	0·553	6·00	11·77	0·400	117
105	0·98	4·01	6·51	8·02	7·58	0·530	5·79	13·37	0·413	118
125	0·19	4·80	5·72	9·59	9·02	0·513	5·58	14·60	0·421	120
145	0·03	4·96	5·56	9·93	9·34	0·510	5·57	14·91	0·422	113

$m = 1·543$. Mean = 116

The data of the other five experiments gave constants of the same order of agreement, and are here summarised.

Expt.	a.	l.	α.	$H'_P = h$.	m.	$k\times10^5$.
II.	9·80	20·62	0·552	11·81	1·546	148
IV.	9·92	5·34	0·735	4·07	1·651	134
V.	9·86	10·44	0·645	7·05	1·606	124
VI.	2·43	25·50	0·525	13·91	1·425	139
VII.	2·46	13·00	0·622	8·40	1·507	120

[In experiment VII, the complete formula (10) was used with $n=0·030$.]

The following experiment is comparable with I, and shows the negligible effect of adding more potassium iodide (see p. 1327):

XII.	4·97	10·44	0·650	7·05	1·566	114

The next thirteen experiments were with initial hydrochloric acid. Only experiments III and XVI are given in detail, the latter showing the accuracy of the constant at very low concentrations of iodine.

Experiment III.

t.	$a-s$.	s.	$l-s$.	HI.	H'_{HI}.	α.	H'_P.	h.	$1-\alpha_M$.	$k\times10^5$.
0	4·93	—	10·44	11·30	10·59	0·496	5·38	15·97	—	—
5	4·33	0·60	9·84	12·51	11·68	0·485	5·26	16·94	0·510	(139)
10	3·89	1·04	9·40	13·38	12·47	0·478	5·18	17·65	0·513	126
15	3·34	1·59	8·85	14·48	13·47	0·470	5·10	18·57	0·517	129
20	2·80	2·13	8·31	15·56	14·44	0·463	5·02	19·46	0·520	130
25	2·31	2·62	7·82	16·55	15·35	0·457	4·95	20·30	0·524	129
30	1·81	3·12	7·32	17·55	16·24	0·450	4·88	21·12	0·527	130
35	1·40	3·53	6·91	18·37	16·97	0·445	4·82	21·79	0·530	127
40	0·95	3·98	6·46	19·25	17·75	0·439	4·76	22·51	0·533	128
45	0·57	4·36	6·08	20·02	18·44	0·434	4·70	23·14	0·535	128
50	0·28	4·65	5·79	20·60	18·95	0·430	4·66	23·58	0·537	128
55	0·11	4·82	5·62	20·94	19·26	0·428	4·64	23·90	0·538	128
60	0·04	4·91	5·53	21·12	19·41	0·426	4·62	24·03	0·539	130

$m = 1·644$. Mean = 128

Experiment XVI.

t.	$a-s$.	s.	$l-s$.	HI.	H'_{HI}.	α.	H'_P.	h.	$1-\alpha_M$.	$k\times10^5$.
0	0·499	—	2·670	14·10	13·13	0·515	1·43	14·56	—	—
2	0·460	0·039	2·631	14·18	13·20	—	1·42	14·62	0·486	(135)
7	0·389	0·110	2·560	14·32	13·33	—	1·42	14·75	—	116
12	0·319	0·180	2·490	14·46	13·47	—	1·42	14·89	—	116
16	0·267	0·232	2·438	14·57	13·56	—	1·41	14·97	—	116
22	0·196	0·303	2·367	14·71	13·68	—	1·40	15·08	—	116
28	0·141	0·358	2·312	14·82	13·79	—	1·40	15·19	—	116
44	0·043	0·456	2·214	15·01	13·96	0·503	1·39	15·35	0·491	116

$m = 1·73$. Mean = 116

Expt.	a.	l.	HI.	H'_{HI}.	α.	H'_P.	m.	$k\times10^5$.
XIV.	9·76	10·30	11·10	10·41	0·498	5·33	1·647	128
XV.	0·250	2·670	28·20	25·66	0·409	1·13	1·830	136
XVII.	0·250	2·670	14·10	13·13	0·515	1·43	1·764	132
XVIII.	0·986	1·040	28·0	25·5	0·415	0·45	1·66	123
XIX.	9·58	20·20	10·86	10·19	0·459	9·64	1·572	145
XX.	0·985	2·080	28·0	25·5	0·412	0·9	—	122
XXI.	0·985	2·080	11·20	10·47	0·550	1·20	1·81	112
XXII.	0·493	1·040	28·0	25·5	0·415	0·44	—	137
VIII.	4·97	2·67	113·0	96·0	0·25	—	—	137
IX.	2·485	2·67	56·5	51·0	0·30	—	—	129
XI.	2·485	2·67	113·0	96·0	0·25	—	—	131

Where no value is given for m, h is regarded as constant, and in the last three experiments the value of H'_P has been neglected, as not appreciably affecting the total value of h. Also, in the last three experiments, α was obtained by extrapolation, and is therefore only approximate.

In experiment XI, eight values, all between 300 and 312, were obtained for the constant $k''\times10^4$ mentioned on p. 1327. In experiment XX, similarly all ten values were between 107 and 112.

The following seven experiments were in a solution molar with respect to both phosphoric acid and potassium dihydrogen phosphate as "regulator" (see p. 1326). Formula (13) is used in each case. Experiment XXIII is given in detail.

Experiment XXIII.

t.	$a-s$.	s.	$l-s$.	$k'\times10^4$.
0	4·996	—	10·50	—
2	4·596	0·400	10·10	274
6	3·898	1·098	9·40	267
10·2	3·246	1·750	8·75	268
15	2·578	2·418	8·08	272
20	1·996	3·000	7·50	274
25	1·522	3·474	7·03	274
33	0·950	4·046	6·40	276
45	0·432	4·564	5·94	276

Mean 272

Expt.	a.	l.	$k' \times 10^4$.
XXIV.	4·970	5·224	271
XXV.	2·494	5·250	254
XXXI.	0·4992	1·050	264
XXXII.	0·2496	1·050	291
XXXIII.	0·4992	0·525	266
XXXIV.	0·4994	5·250	240

For XXV, all eight values of $k'' \times 10^4$ (p. 1327) are between 600 and 626.

Experiment XXVI was exactly comparable with XXV, except that it contained potassium iodide in the proportion of 15·8 molecules to each molecule of iodine; XXV, and all other experiments except XII, have the proportion 3·76. The constant, $k' \times 10^4$, was 255; the agreement with 254, obtained in XXV, shows that iodine functions as the I_3' ion.

Experiment XXVII, at 11·6°, gave a constant, $k' \times 10^4 = 54·8$, and as it is exactly parallel with XXV, the temperature-coefficient is 4·64 for 13·4 degrees. Logarithmic proportion reduces this to 3·14 for 10 degrees and 2·22 for 7 degrees. Steele found 3·1 for 10 degrees for solutions without added acid or "regulator." Since the term involving r', the ratio between two rapid reaction velocities (see formula 12), accounts for more than half the value of the constants, it appears that this ratio is practically unaltered over the range of temperature employed.

The agreement between the constants obtained in this series of "regulator" experiments shows clearly that the iodine must function in the manner shown in the equations used. The effect of neglecting it is very much more apparent in this series than in the earlier experiments.

In order to detect possible oxidation to phosphoric acid, the following procedure was adopted. If phosphorous acid only is produced, each molecule of iodine reduced gives rise to 2 molecules of hydriodic acid, and also changes 1 molecule of monobasic hypophosphorous acid to 1 molecule of dibasic phosphorous acid, phenolphthalein being used as indicator; whereas, if phosphoric acid is produced, 2 molecules of iodine give rise to 4 molecules of hydriodic acid, and still only raise the basicity by unity. Therefore, in the former case, the increase of acidity should be 1·5 times the number of equivalents of iodine consumed, and in the latter case the ratio should be 1·25. In every case tested, the ratio has been very close to 1·5, so that the production of phosphoric acid is very slight.

Expt. I.—At t_{145}, 20 c.c. required 14·84 c.c. of N/10-NaOH more than at t_0; iodine consumed = 9·93 c.c. of N/10-$Na_2S_2O_3$; ratio = 1·495.

Expt. II.—Increase of alkali titre at $t_{50}=14{\cdot}63$ c.c.; iodine consumed $=9{\cdot}75$ c.c.; ratio $=1{\cdot}501$.

Expt. V.—Increase of alkali titre at $t_{150}=19{\cdot}58$ c.c.; iodine consumed $=13{\cdot}10$ c.c.; ratio $=1{\cdot}495$.

For the same purpose in the "regulator" series, an experiment (XXVIII) was carried out exactly parallel with XXV, except that hypophosphorous acid was replaced by the same concentration of phosphorous acid. In three hours, less than one-half per cent. of the iodine was reduced, whereas in experiment XXV, 50 per cent. was reduced in twenty-two minutes.

Experiment X was carried out with hypophosphorous acid which was previously neutralised (to methyl-orange), and is comparable with I. In five hours, less than 5 per cent. of the iodine was reduced; as the second hydrogen ion of the phosphorous acid, originally present to a slight extent, would be sufficient to start the reaction, and so provide more hydrogen ions, it is probable that reaction in neutral solution is extremely slow, and that the H_2PO_2' ion does not react, except, possibly, in the presence of hydrogen ions, in which case reaction is evidently so slow as not greatly to affect the constancy of values obtained on the assumption that it does not take place at all.

The following experiments of Steele's are quoted, after conversion to the units used herein, to show how the irregularities observed by him are largely accounted for in the light of the present work. The first two columns are derived from his data; the remainder are obtained as in the author's results. The constants obtained by each method are shown, those of Steele being designated by K_s. The letter S after the Roman numerals indicates his experiments.

The value 119 obtained for $k\times10^5$ in X(S) is in agreement with the author's results, and shows less falling off with time than does K_s. Moreover, for the three experiments, the results are far more concordant than those obtained on Steele's hypothesis. The fact that Steele used a very pure specimen of hypophosphorous acid may account for the slightly lower values in his experiments.

Expt.	a.	l.	a.	$H'_P=h$.	$k\times10^5$.	$K_s\times10^3$.
X(S)	2·00	20·00	0·555	11·10	119	94
XI(S)	0·500	5·00	0·734	3·67	92	45
XII(S)	0·200	2·00	0·841	1·68	83	24·5

Although the agreement is not so good as in the other results, it is evidently far better than in the results obtained by Steele's method, so that the present hypothesis, which attributes a definite part to the iodine molecules, is apparently more justified by results than that which ignores the iodine and attributes the great decrease

in the constant to a decreased activity of hypophosphorous acid at low concentrations.

This is further supported by a reconsideration of Steele's experiment II, for which he could not obtain a constant without assuming the degree of ionisation to be 0·20 instead of the actual 0·775, which was again supposed to be due to decreased activity. According to the present method, one obtains moderate constancy.

Experiment II(S) at 18°.

t.	$a-s$.	s.	$l-s$.	H^{+HI}.	a.	H^{+}_{P}.	h.	$1-a_H$.	$k \times 10^5$.
0	4·50	—	4·00	—	0·775	3·11	3·11	—	—
390	4·20	0·30	3·70	0·60	0·750	3·00	3·60	0·235	(25·3)
570	3·98	0·52	3·48	1·02	0·735	2·94	3·96	0·245	(28·1)
1440	2·42	2·08	1·92	4·00	0·660	2·64	6·64	0·280	38·3
1710	2·04	2·46	1·54	4·68	0·643	2·56	7·24	0·290	37·7
1830	1·84	2·66	1·34	5·04	0·636	2·54	7·58	0·295	39·2
2805	0·80	3·70	0·30	6·96	0·597	2·38	9·34	0·340	41·5
3240	0·68	3·82	0·18	7·24	0·592	2·36	9·60	0·355	39·8
							m = 1·675.	Mean =	39·3

If the temperature-coefficient for seven degrees is taken as 2·22 (see p. 1332), this gives the low value of 87 for 25°, but, that the experiments correspond in general is seen from the following summary of experiments, for which the data can be utilised:

Experiment.	III(S).	IV(S).	V(S).	VIII(S).	XIII(S).	XV(S).	XXI(S)
$k \times 10^5$	108	115	119	105	107	113	119
$K_S \times 10^4$	355	400	425	430	425	505	555

Steele's $K_S \times 10^4$, given for comparison, clearly shows the inadequacy of his hypothesis.

The method of treatment now presented obviously places the question on a more systematic basis, although the slight variation of the "constant" from one experiment to another is not accounted for; but the several small approximations made, together with the uncertainty in the choice of the value of the constant r, the large influence, in certain cases, of a difference, $l-a$, which is sometimes very small, and the alteration in the proportion of the iodine which is present as the I_3' ion, may easily account for the variation of 10 per cent. from the mean value, 128×10^{-5}. It is also probable that the H_2PO_2' ions react slowly, and account partly for the variations, since the three highest constants are given by the three greatest concentrations of hypophosphorous acid.

Summary.

(1) The previous attempt to explain the reaction had suggested an hypothesis involving the presence of free ionic charges. By taking

into consideration certain factors which had been ignored, this is shown to be unnecessary, and most discrepancies disappear.

(2) These factors were: (i) the influence of the iodine concentration on the measurable velocity, this influence being slight at moderate dilution, but relatively large at greater dilution, and (ii) the effect of hydrochloric and hydriodic acids on the ionisation of hypophosphorous acid.

(3) The following hypothesis is advanced to explain all the anomalies formerly noted. The hypophosphorous acid *molecules* are in equilibrium with a very small proportion of an "active" form (say H_5PO_3), which reacts rapidly with the iodine,

$$H_5PO_3 + I_3' \longrightarrow H_3PO_3 + 2H^* + 3I'.$$

The restoration of the equilibrium thus displaced is accelerated by hydrogen ions, and forms the measurable reaction,

$$H_3PO_2 + H_2O \rightleftharpoons H_5PO_3.$$

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CXLIII.—*Modification and Extension of the Friedel and Crafts' Reaction. Part I.*

By JNANENDRA NATH RÂY.

RADZIEWANOWSKI (*Ber.*, 1895, **28**, 1139) suggested some modifications of the Friedel-Crafts' reaction, in one of which he used a mixture of aluminium powder and mercuric chloride. He prepared ethylbenzene in small yield, but did not obtain any triphenylmethane in the condensation of chloroform and benzene. Von Gulewitsch (*Ber.*, 1904, **37**, 1560) studied the interaction of mercuric chloride and aluminium in benzene, and isolated a compound, $C_6H_6,AlCl_3,HgCl$. A similar compound was formed with toluene. It was thought that if this double compound were employed as a catalyst, the secondary changes that rendered Radziewanowski's reaction unsuccessful might disappear. This expectation has been amply realised. Von Gulewitsch showed the course of the reaction to be

$$C_6H_6 + Al + 2HgCl_2 \longrightarrow C_6H_6,AlCl_3,HgCl + Hg.$$

The mercury, liberated as above, forms an amalgam with the unchanged aluminium, but when an excess of mercuric chloride is employed, this tendency to amalgamate is reduced, inasmuch as

the whole of the aluminium is utilised in reducing mercuric to mercurous chloride. The success of the reaction depends on the non-formation of the amalgam, as otherwise it acts concurrently with the double compound.

Some interesting products have been isolated in the condensation of the hydrocarbons with chloroform, carbon tetrachloride, benzylidene chloride, etc. Thianthren has been prepared in an 80 per cent. yield from benzene and sulphur. This compound was obtained in small amount along with phenyl mercaptan, phenyl sulphide, and phenyl disulphide by Friedel and Crafts (*Ann. Chim. Phys.*, 1888, [vi], **14**, 438) in the condensation of benzene and sulphur with aluminium chloride, whilst Genvresse (*Bull. Soc. chim.*, 1897, [iii], **17**, 599) observed the formation of thianthren and *iso*thianthren in the same reaction.

9:10-Diphenyl-9:10-dihydroanthracene is formed by the condensation of benzene and chloroform, whilst in the ordinary Friedel-Crafts' reaction (*Annalen*, 1878, **194**, 254; 1885, **227**, 107), triphenylmethane, chloroarylmethanes, and tetraphenylethane (*Ber.*, 1893, **26**, 1952) are the products. The same compound is obtained by the interaction of benzylidene chloride and benzene.

Carbon tetrachloride and benzene give 9:9:10:10-*tetraphenyl*-9:10-*dihydroanthracene*, which is also obtained from benzotrichloride and benzene, whilst in the usual reaction, triphenylmethane, chloroarylmethanes (*Annalen*, 1878, **194**, 254), and tetraphenylethylene (*Ber.*, 1893, **26**, 1952) are obtained.

Similarly, *dimethyl*-9 : 10-*ditolyl*-9 : 10-*dihydroanthracene* has been obtained from chloroform and toluene. In this condensation, using aluminium chloride, Schwarz (*Ber.*, 1881, **14**, 1530) prepared tetratolylethane, which has the same melting point (215°) and empirical formula, but a mixture of the two melts at 206—208°. Benzylidene chloride and toluene yield *dimethyl*-9:10-*diphenyl*-9:10-*dihydroanthracene*.

Finally, chloropicrin and benzene, under the action of the reagent, furnish ω-nitrotriphenylmethane, previously obtained by the direct addition of nitrogen peroxide to triphenylmethyl (Schlenk, Mair, and Bornhardt, *Ber.*, 1911, **44**, 1172). Boedtker (*Bull. Soc. chim.*, 1908, [iv], **3**, 726) states, however, that all aliphatic nitro-compounds lose their nitro-groups under the influence of aluminium chloride, and obtained triphenylmethane and some triphenylcarbinol in this reaction.

Experimental.

To a mixture of 20 c.c. of dry benzene and 20 grams of mercuric chloride contained in a flask with reflux condenser, 1 gram of aluminium powder was added gradually, and the flask vigorously shaken. The heat of the reaction caused the benzene to boil, and the flask was occasionally cooled in an ice-bath. A green, crystalline mass eventually separated, and the reaction was completed by immersing the flask in tepid water for half an hour. The mercury liberated in the reaction was removed, and the preparation of the catalyst was complete.

In all the reactions described below, the components were well agitated by a mechanical stirrer.

Acetophenone.—The calculated amount (1 mol.) of acetyl chloride was added through the condenser in small quantities at a time, the mixture allowed to remain for two hours at the ordinary temperature, and then heated to 40° for an hour. On cooling, it was decomposed with water, and the oil extracted with benzene, the benzene solution being dried and finally fractionated. The yield of acetophenone was 60 per cent. of the theoretical, whilst by Friedel and Crafts' method it is 55·5 per cent.

p-*Tolyl Methyl Ketone.*—Following an almost identical method, from 33 c.c. of toluene, 2·5 grams of aluminium, and 45 grams of mercuric chloride, 16·1 grams of this ketone were obtained.

Thianthren, $C_6H_4\langle{}^{S}_{S}\rangle C_6H_4$.—The catalyst was prepared from 2·5 grams of aluminium, 45 grams of mercuric chloride, and 30 c.c. of benzene; 10 grams of flowers of sulphur were added, and the mixture was heated on the water-bath until hydrogen sulphide was no longer evolved. The product, on cooling, was decomposed with ice, filtered, and the residue repeatedly extracted with chloroform, from which the substance was obtained on concentration. When crystallised from acetone, it melted at 160°. The yield was 14 grams (Found: C = 66·1; H = 3·8; S = 28·5. Calc.: C = 66·6; H = 3·7; S = 29·6 per cent.).

9 : 10-*Diphenyl*-9 : 10-*dihydroanthracene.*—The catalyst was prepared from 1 gram of aluminium, 20 grams of mercuric chloride, and 15 c.c. of benzene. Six c.c. of chloroform were added drop by drop through the condenser, and the flask was allowed to remain at the ordinary temperature for two hours, and then heated for an hour at 40°, and then for another hour at 40—50°. On cooling, the product was decomposed with ice and filtered. There separated from the filtrate a deep red oil, from which some unchanged benzene was evaporated. The residue was extracted with

boiling acetic acid containing a little water, from which the compound separated on cooling. After being crystallised from dilute alcohol, and then repeatedly from dilute acetone, the compound melted at 159° (Linebarger, *Amer. Chem. J.*, 1891, **13**, 556, gives 164·2°) (Found: C = 93·2; H = 6·7. Calc.: C = 93·9; H = 6·1 per cent.).

The same compound was obtained by the interaction of 3 c.c. of benzylidene chloride, 8 c.c. of benzene, 0·5 gram of aluminium, and 10 grams of mercuric chloride, the reaction being completed at 50—55°. The product was isolated as described above (Found: C = 94·0; H = 6·39. Calc.: C = 93·9; H = 6·1 per cent.). A solution of 1 gram of the substance in acetic acid was oxidised with an acetic acid solution of chromium trioxide, and the product poured into water. The resinous mass was dried and then sublimed, and the sublimate was proved to be anthraquinone by the method of mixed melting points.

The *diacetyl* derivative was prepared by heating 1 gram of the substance with 10 c.c. of acetic anhydride and four drops of pyridine under reflux for an hour. The product was poured into water and neutralised with sodium carbonate. The viscous mass solidified, and, after being fractionally crystallised from dilute alcohol, melted at 92° (Found: C = 85·3; H = 7·4. $C_{28}H_{24}O_2$ requires C = 85·7; H = 6·8 per cent.).

Dimethyl-9 : 10-*ditolyl*-9 : 10-*dihydroanthracene*.—This condensation was performed as in the preceding case, the catalyst being prepared from 1 gram of aluminium, 20 grams of mercuric chloride, and 15 c.c. of toluene. Chloroform (1 mol. for 2 mols. of toluene) was added through the condenser, and finally the reaction was completed at 70°. The oily product obtained after the decomposition of the mixture with ice, after being freed from chloroform and toluene, solidified when kept in a vacuum desiccator, and when crystallised from dilute acetic acid melted at 215° (Found: C = 92·0; H = 7·9. $C_{30}H_{28}$ requires C = 92·7; H = 7·3 per cent.).

Dimethyl-9 : 10-*diphenyl*-9 : 10-*dihydroanthracene*.—The catalyst, prepared from 8 c.c. of toluene, 0·5 gram of aluminium, and 10 grams of mercuric chloride, was treated with 4 c.c. of benzylidene chloride, the reaction being completed by heating at 60—70° for two hours. The oily product obtained after the usual treatment was dried and distilled under diminished pressure, when some oily matter passed over, and the residue solidified. This was extracted with hot alcohol, and, on concentration, a product was obtained which, after crystallisation from acetic acid, melted at 185° (Found: C = 92·8; H = 7·0. $C_{28}H_{24}$ requires C = 93·3; H = 6·7 per cent.).

9:9:10:10-*Tetraphenyl*-9:10-*dihydroanthracene*.—Eight c.c. of carbon tetrachloride were added to the catalyst, prepared from 20 c.c. of benzene, 1 gram of aluminium, and 20 grams of mercuric chloride, and the whole was kept at 50—60° for two hours, and then at 70° for an hour. After decomposing the product with ice and filtering, the dried residue was extracted with carbon disulphide, from which some of the tetraphenyl derivative was obtained. The filtrate separated into two layers, and the benzene layer, on evaporation, gave a further quantity of the substance, which, when crystallised from dilute acetone, melted at 159° (Found: C=94·0; H=6·8. $C_{38}H_{28}$ requires C=94·2; H=5·8 per cent.). The same compound was obtained by adding 5 c.c. of benzotrichloride, in the course of half an hour, to the catalyst, prepared from 15 c.c. of benzene, 1 gram of aluminium, and 20 grams of mercuric chloride. The product, isolated as above, melted at 159° (Found: C=94·02; H=5·1. Calc.: C=94·2; H=5·8 per cent.).

ω-*Nitrotriphenylmethane*.—Five c.c. of chloropicrin were used with 20 c.c. of benzene. The mixture was warmed first in a tepid-water bath and then for a few hours at 45°. The product was decomposed with ice, distilled in a current of steam, and the residue filtered, dried, and extracted with much boiling alcohol. This, on concentration, deposited ω-nitrotriphenylmethane, which, on recrystallisation from alcohol, melted and decomposed at 145° (Found: C=78·49; H=5·54; N=4·5. Calc.: C=78·8; H=5·1; N=4·8 per cent.).

In conclusion, I wish to express my best thanks to Sir P. C. Rây for the interest he has taken in the work, and to Mr. M. L. Dey for his criticisms and suggestions.

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CXLIV.—*The Freezing Point of Wet Benzene, and the Influence of Drying Agents.*

By Nevil Vincent Sidgwick.

During the purification of benzene by freezing for cryoscopic purposes, irregularities were observed in the freezing points of successive fractions, which were found to be due to traces of water absorbed from the air. This suggested the determination of the maximum depression of the freezing point of benzene by water. In a previous paper (T., 1915, **107**, 675), it was stated that this depression amounts to 0·042°, but later work has shown that the readiness with which benzene absorbs water from the air had been underestimated, and that the original benzene was not really dry. If proper precautions are taken to dry the benzene, its freezing point is lowered 0·100° by the addition of excess of water.*

This affords a convenient method for determining the efficiency of various drying agents. If the wet benzene is shaken with a solid dehydrating agent, which is insoluble in it, until a constant freezing point is obtained, the ratio of the depression observed in the presence of the drying agent to that produced by pure water is a measure of the lowering of the vapour pressure of the water by the latter, and hence of the efficiency of the drying agent. This efficiency must be the same (at temperatures near 5°) for a solution in any solvent in which the drying agent is insoluble.

Experimental.

Two samples of benzene, each about a litre, were used: one (*A*) was kindly given me by Dr. Hewitt and Mr. W. J. Jones; it was of English origin, and had been purified by them. The other (*B*) was Kahlbaum's purest. Neither gave more than the faintest trace of the indophenine reaction.

These were further purified separately by repeated freezing. In the later stages, irregularities of several hundredths of a degree were observed in the freezing points, which disappeared when the measurements were made in the presence of potassium carbonate.

When the freezing points appeared to be constant, the benzene

* After this work was finished, a paper appeared by Richards, Carver, and Schumb (*J. Amer. Chem. Soc.*, 1919, **41**, 2024), in which two experiments are described on the depression of the freezing point of pure benzene by water, giving the values 0·093° and 0·096°: mean 0·095°. This is in satisfactory agreement with the value 0·100° adopted in the present paper.

was still further purified by the method described by Richards and Shipley (*J. Amer. Chem. Soc.*, 1914, **36**, 1825) and by Richards and Barry (*ibid.*, 1915, **37**, 993). It was boiled for some hours with clean sodium (previously washed with the benzene) in a flask with a bent reflux condenser and drying tube. The condenser was then inclined downwards and connected to the side-tube of a carefully dried Beckmann apparatus. A steady stream of dried air was passed into the apparatus through the sheath of the stirrer, which was expanded into a bulb in the usual way, to prevent moist air from being drawn in when the stirrer was raised. It is essential that the access of moist air should be prevented; in one experiment the condenser tube was accidentally separated from the Beckmann apparatus for a minute, and this caused a drop in the freezing point of several thousandths of a degree. To the condenser tube between the water-jacket and the freezing-point apparatus, a rather narrow side-tube was sealed, so as to point downwards when the condenser was in position for distillation. The first runnings escaped through this tube, which was then closed by attaching a test-tube to it with an air-tight cork. The tube then filled up with liquid, and the rest of the distillate ran straight into the freezing-point apparatus.

Several readings of the freezing point having been taken, two or three drops of water were added, the tube was warmed with the hand and well stirred, and the freezing point again observed. This gave the difference between the freezing point of pure benzene and that of benzene saturated with water (the triple point, solid benzene–liquid benzene–water). Then about half a gram of dry, powdered potassium carbonate was added and thoroughly stirred, and the freezing point again taken. A smaller quantity of the salt was then added in the same way, and if this raised the freezing point, another small quantity was added; more than three additions were never required. This gives the temperature of the quadruple point, solid benzene–solid potassium carbonate–benzene solution–saturated aqueous solution of potassium carbonate. These operations were performed with successive frozen-out fractions of the purified benzene, and the results are given in the following table. The temperatures are referred to the arbitrary zero of the Beckmann thermometer, which remained constant during the experiments; each is the mean of several concordant readings, corrected for the temperature of the emergent stem. The fractions marked *A* are the English benzene, *B* the German; the index number following this shows the number of times it had been frozen out; thus, *A* 7 is the fraction obtained by freezing out the English benzene seven times.

Fraction.	I. Dried by sodium.	II. With water.	III. Wet, with potassium carbonate.	I.—II.	III.—II.
A 7	3·120°	3·021°	3·080°	0·099°	0·059°
A 7	3·121	3·021	3·081	0·100	0·060
A 8	—	3·023	3·083	—	0·060
A 9	3·119	3·021	—	0·098	—
B 6	3·115	3·015	3·075	0·100	0·060
B 7	—	3·020	3·081	—	0·061
B 8	3·121	3·022	—	0·099	—
B 8	—	3·022	3·081	—	0·061
Means			*A*....	0·099	0·060
			B....	0·100	0·061

The freezing point is thus lowered 0·100° by saturation with water. If the molecular weight of the dissolved water is 18, its solubility at 5·4° (assuming the cryoscopic constant 51°) must be 0·035 gram per 100 grams of benzene. Groschuff (*Zeitsch. Elektrochem.*, 1911, **17**, 348) found that 100 grams of benzene at 3° dissolve 0·030 gram of water, and at 23° 0·061, which would mean about 0·032 gram at 5·4°, agreeing with the observed depression for a molecular weight of 18. The value 0·24 gram in 100 grams at 22° given by Herz (*Ber.*, 1898, **31**, 267) is presumably erroneous.

On the addition of potassium carbonate, water is withdrawn from the benzene to form a saturated solution of the salt, the vapour pressure of which is lower than that of pure water; the concentration of the benzene solution diminishes and its freezing point rises by 0·061°, being 0·039° lower than that of pure benzene.

Other dehydrating agents were then examined in the same manner. Carefully dried and powdered specimens of sodium sulphate, copper sulphate, and calcium chloride were used, and also powdered sodium hydroxide and pure phosphoric oxide; this last blackens rapidly in impure benzene, but remains quite colourless in the pure liquid. All these compounds differ from potassium carbonate in forming hydrates with the water, and it is perhaps for this reason that some of them, especially copper sulphate, act more slowly, and must be stirred with the liquid for some time before their full effect appears. In these experiments, the benzene was not in each case distilled over sodium, but a mixture of the fractions *A* 9 and *B* 8, which had been so treated, was saturated with water, and after its freezing point had been measured it was dried with the salt, and the rise of freezing point so produced was observed.

Drying agent.	Elevation of freezing point.	Depression by water + agent.
None	—	0·100°
Sodium sulphate	0·024°	0·076
Potassium carbonate	0·061	0·039
Copper sulphate	0·089	0·011
Calcium chloride	0·091	0·009
Sodium hydroxide.....	0·098	0·002
Phosphoric oxide	0·100	0·000

The removal of water by phosphoric oxide seems to be quite complete.

The middle column in the above table gives a measure of the relative efficiency of the drying agents examined. If water in benzene solution is unimolecular, its concentration in the solution is proportional to the pressure of its vapour, and hence the depression given in the last column is directly proportional to the vapour pressure of the system, drying agent–lowest hydrate (or saturated solution in the case of potassium carbonate)–vapour.

The last column in the following table gives the values of the tension of aqueous vapour calculated on this hypothesis. The preceding column gives the actual freezing points, based on the revised value given by Richards, Carver, and Schumb (see footnote on p. 1340) for pure benzene.

System.	Freezing point.	Tension of aqueous vapour in mm.
Benzene, pure	5·493°	—
„ saturated with water ...	5·393	6·73
„ wet + sodium sulphate...	5·420	5·11
„ „ + potassium carbonate	5·454	2·62
„ „ + copper sulphate ...	5·482	0·74
„ „ + calcium chloride ...	5·484	0·61
„ „ + sodium hydroxide	5·491	0·13
„ „ + phosphoric oxide .	5·493	0·00

The relative efficiency of these substances is, of course, the same for drying solutions in any other solvents in which they do not dissolve.

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CXLV.—*Studies in the Acenaphthene Series. Part I. The Conversion of* o-*Nitroamines into* iso*Oxadiazole Oxides.*

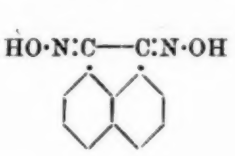
By Frederick Maurice Rowe and John Stanley Herbert Davies.

In four previous communications (T., 1912, **101**, 2452; 1913, **103**, 897, 2023; 1917, **111**, 612), one of us has shown that many *o*-nitroamines in the benzene and naphthalene series are converted into furoxans (furazan oxides or *iso*oxadiazole oxides) when oxidised in alkaline solution with sodium hypochlorite. In order further to test the generality of this reaction, we have now carried out similar experiments in the acenaphthene series. Sachs and Mosebach (*Ber.*, 1911, **44**, 2852) have shown that whilst the direct nitration of acenaphthene yields a dinitro-derivative which contains the nitro-groups in the 3:4- or peri-position, the reduction of 3-nitroacenaphthene, followed by acetylation, nitration, and hydrolysis of the resulting nitroacetylaminoacenaphthene, gives rise to 2-nitro-3-aminoacenaphthene. The latter compound, which contains the nitro- and amino-groups in the ortho-position with respect to one another, has now been submitted to the hypochlorite oxidation. It is interesting to note that, although the yield of the oxidation product was low, the methylene groups of the acenaphthene ring remained unaffected, and *acenaphthene*-2:3-iso*oxadiazole oxide* was obtained. The corresponding compounds in the benzene and naphthalene series possess a characteristic almond odour, and are readily volatile with steam, but this compound is odourless and non-volatile. It is reduced by hydroxylamine to *acenaphthene*-2:3-*quinonedioxime*, which may be converted into *acenaphthene*-2:3-iso*oxadiazole* in the usual manner, although the yield is not good.

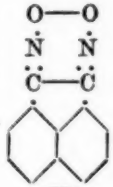
An attempt to reduce 2-nitro-3-acetylaminoacenaphthene to the corresponding nitroso-compound in a similar manner to that used by one of us for the preparation of *o*-nitrosoacetanilide (*loc. cit.*), in order to prepare acenaphthene-2:3-*iso*oxadiazole from it by the alkaline hypochlorite oxidation, proved unsuccessful.

o-Quinonedioximes are readily converted into *iso*oxadiazole oxides by oxidation in alkaline solution with sodium hypochlorite, and consequently it was to be expected that the oxidation of acenaphthene-7:8-quinonedioxime in this manner would yield an *iso*oxadiazole oxide derivative of acenaphthene of a different type

from that already described. This, in fact, proved to be the case, and *acenaphthene*-7 : 8-iso*oxadiazole oxide* was obtained. On the other hand, acenaphthene-7 : 8-quinonedioxime resisted all attempts to convert it into acenaphthene-7 : 8-*iso*oxadiazole by the removal of water. It remained unaffected by prolonged boiling with aqueous sodium hydroxide, and when heated with aqueous sodium hydroxide in a sealed tube, decomposition occurred, with the formation of acenaphthenequinone and ammonia, whilst no better result was obtained by heating with water in a sealed tube. Moreover, treatment of the diacetyl derivative of acenaphthene-7 : 8-quinonedioxime with sodium hydroxide merely resulted in hydrolysis, with no dehydration. This failure to dehydrate acenaphthene-7 : 8-quinonedioxime suggests that this compound most probably has the structure of a β(anti)-dioxime (I). The failure of this compound



(I.)



(II.)

to give a nickel salt when treated with ammoniacal nickel solutions, as described by Atack (T., 1913, **103**, 1317) in an investigation of the three stereoisomeric benzildioximes, further supports this view.

The preparation of acenaphthene-7 : 8-*iso*oxadiazole oxide was of interest in view of the fact that Francesconi and Pirazzoli (*Gazzetta*, 1903, **33**, i, 36) prepared a compound by boiling acenaphthene-7 : 8-quinonedioxime with amyl nitrite, to which the peroxide formula (II) was provisionally assigned. This compound is described as forming reddish-brown crystals, decomposing at 90° and melting at 140°. It is soluble in organic solvents, with decomposition, forming a black substance which does not melt at 260°. We therefore prepared a quantity of this compound in order to determine whether it was identical or not with acenaphthene-7 : 8-*iso*oxadiazole oxide. After repeated crystallisation, it was obtained finally in small, brown needles, decomposing at 190° and melting at 206·5°, and, when pure, it was not decomposed by organic solvents. This substance possesses quite different properties from those of acenaphthene-7 : 8-*iso*oxadiazole oxide; for example, the former dissolves in cold aqueous sodium hydroxide with a pale yellow colour, whilst the latter is quite insoluble in alkali hydroxides, and, moreover, is readily reduced to acenaphthene-7 : 8-quinonedioxime by hydroxylamine. It is evident that the two

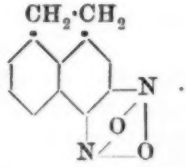
compounds are not identical, and Francesconi and Pirazzoli's compound was not examined more closely, but, in view of its properties, it seemed doubtful whether it possesses the peroxide formula assigned to it by these authors.

When the present investigation was commenced, the literature contained no reference to nitro-derivatives of acenaphthenequinone, and it was decided to fill in this blank. After the necessary experiments had been carried out, however, these compounds were described by Mayer and Kauffmann (*Ber.*, 1920, **53**, [*B*], 296).

The product of mononitration is 3-nitroacenaphthenequinone melting at 218° (M. and K. give 199°), which forms a monophenylhydrazone melting at 234—235° (M. and K. give 186°), and the product of dinitration is 3:4-dinitroacenaphthenequinone melting and decomposing above 300°, which forms a *monophenylhydrazone* darkening at 260° and melting at 287°.

In conclusion, it appeared of interest to ascertain whether the nitro-derivatives of acenaphthenequinone could be prepared by the oxidation of the nitro-derivatives of acenaphthene, as the preparation of a substituted acenaphthenequinone by the oxidation of the corresponding derivative of acenaphthene has been effected only in one instance, namely, by Graebe (*Annalen*, 1903, **327**, 77), who found that 5-bromoacenaphthene was oxidised either to bromoacenaphthenequinone or bromonaphthalic acid, according to the conditions used. Experiments were made with 3-nitroacenaphthene, using a series of oxidising agents under a variety of conditions, but it was found that this compound either remained unaffected or was oxidised to 4-nitronaphthalene-1:8-dicarboxylic acid melting, as anhydride, at 229—230° (Graebe gives 220°), and in no case could we isolate any 3-nitroacenaphthenequinone.

Experimental.

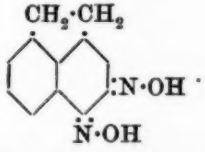
Acenaphthene-2:3-isooxadiazole Oxide,  .

The 2-nitro-3-aminoacenaphthene required was obtained by Sachs and Mosebach's method (*loc. cit.*). Acenaphthene (m. p. 96°) was nitrated in glacial acetic acid suspension, and the product extracted with light petroleum (b. p. 90°), in which any dinitro-derivative formed simultaneously is insoluble. The yield of 3-nitroacenaphthene, yellow needles, melting at 101—102°, was 89 per cent. (S. and M. give 84 per cent.). The reduction of the

nitro-compound is best effected in aqueous-alcoholic solution with sodium hyposulphite. The yield of 3-aminoacenaphthene, almost colourless, silky needles melting at 104—105°, was 71 per cent. (S. and M. give about 77 per cent. of an almost pure product). The monoacetyl derivative is best prepared with acetyl chloride. After repeated crystallisation from methyl alcohol, 3-acetylaminoacenaphthene, glistening needles melting at 238°, was obtained in a yield of 92 per cent. The melting point of this compound is greatly affected by traces of impurities; thus Quincke (*Ber.*, 1885, **21**, 1457) gives 176°, Graebe (*Annalen*, 1903, **327**, 77) gives 186°, and Sachs and Mosebach (*loc. cit.*) give 192°. A number of nitrations were carried out, but the yield was always low, owing to oxidation; 2-nitro-3-acetylaminoacenaphthene, golden-yellow needles melting at 255°, was obtained in a yield of 35 per cent. (S. and M. give 253°; yield, about 54 per cent.). When hydrolysed with alcoholic hydrochloric acid, 2-nitro-3-aminoacenaphthene, blunt, red prisms with a green lustre, melting at 222°, was obtained in an almost theoretical yield (S. and M. give 85 per cent.).

The oxidation of 2-nitro-3-aminoacenaphthene was best effected by the addition of an excess of alkaline sodium hypochlorite to a hot alcoholic solution of the nitroamine. The mixture was boiled for a short time, cooled, diluted with water, and the precipitate collected. When crystallised from alcohol or acetic acid, *acenaphthene*-2:3-iso*oxadiazole oxide* forms pale brown needles melting at 177—178°. A yield of 50 per cent. was obtained. The compound is odourless, non-volatile with steam, and, when heated with zinc dust, ammonia is evolved and naphthalene formed (Found: N = 13·32. $C_{12}H_8O_2N_2$ requires N = 13·2 per cent.).

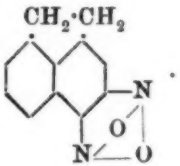
Acenaphthene-2:3-*quinonedioxime*,



This compound was formed by the reduction of acenaphthene-2:3-*iso*oxadiazole oxide with an excess of hydroxylamine (at least four molecular proportions). It was difficult to isolate, owing to the ease with which it was converted into acenaphthene-2:3-*iso*-oxadiazole. The best results were obtained by dissolving the *iso*oxadiazole oxide in alcohol and adding an aqueous solution of hydroxylamine hydrochloride, after which the mixture was rendered alkaline with sodium hydroxide at 50° and heated for twenty minutes on the water-bath at 60°. The brown solution was cooled, acidified with acetic acid, and diluted with water. The

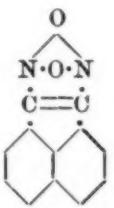
precipitate was extracted with dilute sodium hydroxide, filtered, and the filtrate precipitated with acetic acid. The quinonedioxime separates as a colloidal precipitate, which it was not found possible to crystallise. When dry, it forms a brown, amorphous powder, which decomposes when heated and does not melt below 280°, sparingly soluble in organic solvents, but dissolving readily in alkali hydroxides with a brown colour. On oxidation with sodium hypochlorite, it is reconverted into acenaphthene-2:3-*iso*-oxadiazole oxide, and, on heating with sodium hydroxide, it is converted into acenaphthene-2:3-*iso*oxadiazole (Found: N = 13·34. $C_{12}H_{10}O_2N_2$ requires N = 13·08 per cent.).

Acenaphthene-2:3-iso*oxadiazole*,



Acenaphthene-2:3-quinonedioxime was dissolved in dilute sodium hydroxide and distilled in a current of steam. The product, after recrystallisation from acetic acid, forms yellow needles melting at 143—144°. It is only slightly volatile with steam, and the yield is low, owing to the formation of a large proportion of a black, non-volatile decomposition product (Found: N = 14·45. $C_{12}H_8ON_2$ requires N = 14·28 per cent.).

Acenaphthene-7:8-iso*oxadiazole Oxide*,

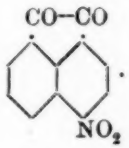


The acenaphthene-7:8-quinonedioxime required was obtained by Francesconi and Pirazzoli's method (*loc. cit.*). Five grams of powdered acenaphthenequinone (m. p. 259°) were suspended in 450 c.c. of boiling alcohol, and 3·8 grams of hydroxylamine hydrochloride dissolved in the minimum quantity of water added. The mixture was boiled for one hour under reflux, and the major portion of the alcohol removed by distillation. The product, colourless needles, melting and decomposing at 220°, was obtained in almost theoretical yield.

An excess of alkaline sodium hypochlorite was added to a solution of acenaphthene-7:8-quinonedioxime in dilute sodium hydr-

oxide, and the mixture boiled. A yellow precipitate separated, which changed in colour through red to pale pink, and boiling was continued until no further colour change occurred. After crystallising twice from alcohol, the compound forms pale pink needles melting at 199°.

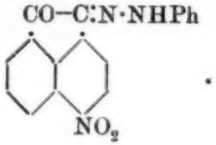
Acenaphthene-7:8-iso*oxadiazole oxide* is reduced by hydroxylamine to acenaphthene-1 : 2-quinonedioxime (Found: N = 12·96. $C_{12}H_6O_2N_2$ requires N = 13·30 per cent.).

3-Nitroacenaphthenequinone, 

Ten grams of acenaphthenequinone, dissolved in 50 c.c. of concentrated sulphuric acid, were nitrated in the cold with one molecular proportion of nitric acid (D 1·51) mixed with twice its volume of concentrated sulphuric acid. At the end of the addition, the mixture was warmed for one hour at 30° and poured on ice. The yield was 92 per cent. Purification by immediate crystallisation proved unsatisfactory, and the best results were obtained by a mild oxidation, which removed the impurities without affecting the nitroquinone. The product (11·5 grams) was dissolved in glacial acetic acid, the solution filtered, and 5 grams of powdered sodium dichromate were slowly added to the filtrate. The mixture was heated on a boiling-water bath for a quarter of an hour and poured into water. After repeated crystallisation from acetic acid, 3-nitroacenaphthenequinone forms yellow needles melting at 218°. It dissolves in sodium hydrogen sulphite with a red colour, and dissolves in dilute alkali hydroxides with a brown colour, whilst it is converted by hot concentrated aqueous sodium hydroxide into 2(or 3)-nitronaphthaldehydic acid, as described by Mayer and Kauffmann (*loc. cit.*).

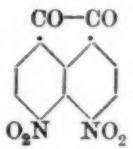
3-Nitroacenaphthenequinone is oxidised by sodium dichromate and acetic acid to 4-nitronaphthalene-1:8-dicarboxylic anhydride, almost colourless needles, melting at 229—230°, identical with the product obtained by a similar oxidation of 3-nitroacenaphthene. When distilled with lime, α-nitronaphthalene is obtained (Found: N = 5·93. Calc.: N = 6·17 per cent.).

3-*Nitroacenaphthenequinone*-7(or 8)-*monophenylhydrazone*,



A cold glacial acetic acid solution of 5 grams of 3-nitroacenaphthenequinone was mixed with a cold glacial acid solution of 2·4 grams of phenylhydrazine, and the dark red mixture was left at the ordinary temperature for half an hour, with frequent shaking. The monophenylhydrazone separates as a maroon-coloured precipitate. After several crystallisations from pyridine, the product forms reddish-brown needles melting at 234—235° (Found: N = 13·22. Calc.: N = 13·25 per cent.).

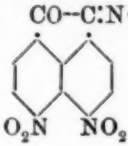
3:4-*Dinitroacenaphthenequinone*,



Ten grams of acenaphthenequinone, dissolved in 150—200 c.c. of concentrated sulphuric acid, were nitrated by the addition of a mixture of 7 c.c. of nitric acid (D 1·51) and 20 c.c. of concentrated sulphuric acid. The mixture was cooled at first, then warmed to 80°, and poured on ice. The product, after extraction with very dilute sodium carbonate, crystallised from nitric acid in orange-yellow needles melting and decomposing above 300°. It dissolves with a red colour, and is soluble in alkali hydroxides with a reddish-brown colour.

3:4-Dinitroacenaphthenequinone is oxidised by sodium dichromate and acetic acid to 4:5-dinitronaphthalene-1:8-dicarboxylic anhydride, almost colourless needles, melting and decomposing above 310°, identical with the product obtained by the oxidation of 3:4-dinitroacenaphthene. No dinitronaphthalene is obtained when distilled with lime, as 1:8-dinitronaphthalene decomposes below its boiling point (Found: N = 10·17. Calc.: N = 10·29 per cent.).

3:4-*Dinitroacenaphthenequinone-7-monophenylhydrazone*,



An acetic acid solution of 2 grams of phenylhydrazine was added to an acetic acid solution of 5 grams of 3:4-dinitroacenaphthenequinone at 50°, and the mixture allowed to remain for one hour at the ordinary temperature. On dilution with water, the product separated as a reddish-yellow precipitate. It crystallises from acetic acid in brown, glistening plates, darkening above 260° and melting at 287° (Found: N = 15·57. $C_{18}H_{10}O_5N_4$ requires N = 15·47 per cent.).

In conclusion, we desire to express our thanks to Messrs. Hardman and Holden, Ltd., who have kindly supplied us with the acenaphthene required in this investigation.

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CXLVI.—*Diethylenetriamine and Triethylenetetramine.*

By ROBERT GEORGE FARGHER.

THE interaction of ethylene dichloride and a large excess of ammonia has been investigated by Kraut (*Annalen*, 1882, **212**, 253), who considered that it led almost entirely to ethylenediamine, although the reaction of the alcohol-soluble portion of the mixed hydrochlorides with potassium bismuth iodide indicated that a small proportion of piperazine was formed.

The author had occasion to prepare several kilograms of ethylenediamine, essentially by Kraut's method, and it was thought to be of interest to investigate in more detail the other products of the reaction. The hydrochlorides obtained by evaporation of the product were converted into the corresponding bases and fractionally distilled. The portion of higher boiling point consisted mainly of diethylenetriamine, whilst there was also produced, although in much smaller quantity, triethylenetetramine. The intermediate

cyclic bases, piperazine and triethylenetriamine, appeared to be absent. Of the two bases isolated, the former was first obtained by Hofmann (*Proc. Roy. Soc.*, 1860, **10**, 619), admixed with triethylenetriamine, by the action of ammonia on ethylene dibromide, and was separated by the more sparing solubility of its platinichloride; the second base he obtained by the interaction of ethylenediamine and ethylene dibromide (*loc. cit.*), ethylene dibromide and alcoholic ammonia (*loc. cit.*), and ethylenediamine and ethylene dichloride (*Ber.*, 1890, **23**, 3712). For purposes of identification and characterisation, a number of derivatives of both have been prepared.

It is of interest to record that the direct union of ethylene with chlorine, utilised in the preparation of the ethylene dichloride required in the present experiments, shows that electrolytic chlorine from a freshly charged cylinder is considerably more active, under identical conditions, than that prepared from bleaching powder. This is in accordance with the view that chlorine is activated by exposure to an electric discharge (compare Kellner, *Zeitsch. Elektrochem.*, 1902, **8**, 500; Russ, *Monatsh.*, 1905, **26**, 627; Briner and Durand, *Zeitsch. Elektrochem.*, 1908, **14**, 706), and that chlorine prepared by electrolysis is more active towards hydrogen (Chapman and MacMahon, T., 1909, **95**, 135).

Contrary to the experience of Russ (*Chem. Ind.*, 1908, **31**, 131), the increased activity is not lost by heating or by contact with water or solutions of such salts as calcium chloride or potassium chlorate. As an example, the fractionation of the products of two experiments may be cited, the results being representative of many others. In the first, using chlorine from bleaching powder, 92 per cent. of the product distilled between 84° and 88°, only 4 per cent. passing over at a higher temperature. In the second, using chlorine from a freshly charged cylinder, only 7 per cent. distilled between 80° and 90°, 25 per cent. passing over between 90° and 100°, 50 per cent. between 100° and 120°, and 14 per cent. above that temperature.

As an alternative to the Kraut process, the reduction of aminoacetonitrile was investigated. The catalytic reduction with hydrogen under pressure in the presence of nickel suboxide had already been claimed to yield ethylenediamine (Brit. Pat. 21883 of 1914). Reduction with sodium and alcohol, zinc and hydrochloric acid, and iron and hydrochloric acid also yielded ethylenediamine, although, as hydrolysis of the nitrile proceeded simultaneously, the yield never exceeded 33 per cent. of the theoretical.

Experimental.

Separation of the Bases.

The bases obtained by distilling the mixed hydrochlorides with solid sodium hydroxide, preferably under somewhat diminished pressure, were freed from water by means of solid sodium hydroxide* and then distilled, first under the ordinary pressure to remove most of the ethylenediamine hydrate, and then under 20 mm. There was first obtained a small fraction boiling below 100° which consisted almost entirely of ethylenediamine, and after this most of the remaining oil passed over between 100° and 120°. The temperature then rose to 155° without remaining constant at any intermediate point, and a fraction was collected boiling between 155° and 165°/20 mm. The first fraction proved to consist almost entirely of diethylenetriamine, which distilled at 109°/20 mm. The second fraction on redistillation boiled at 157°/20 mm., and proved to be triethylenetetramine.

Diethylenetriamine and its Derivatives.

Diethylenetriamine dissolves in water with the evolution of heat and apparent formation of a hydrate. The aqueous solution of the base gives copious, white precipitates with potassium mercuriiodide, mercuric chloride, or phosphotungstic acid, soluble in excess of the base, but no precipitate with tannic acid. It reduces silver nitrate on warming. The alcoholic solution yields an insoluble carbonate when treated with carbon dioxide. Attempts to titrate the base with standard acid, using methyl-orange, Congo-red, litmus, or cochineal as indicator, proved unsuccessful, as no definite end-point could be obtained. For analysis, it was finally distilled over a little solid sodium hydroxide, and was afterwards kept out of contact with moisture or carbon dioxide (Found: C = 46·3; H = 13·1; N = 40·3. Calc.: C = 46·6; H = 12·7; N = 40·75 per cent.).

The trihydrochloride (Hofmann, *Proc. Roy. Soc.*, 1862, **11**, 420) separates from aqueous alcohol containing excess of hydrogen chloride in bunches of feathery needles which melt at 233° (corr.), sintering from 225° (Found: Cl = 50·1, 50·2; N = 19·6. Calc.: Cl = 50·1; N = 19·8 per cent.).

The *tripicrate* is sparingly soluble, even in boiling water, and crystallises in glistening, flattened prisms which melt and decom-

* It is not sufficient simply to distil over sodium hydroxide.

pose at 212° (corr.) (Found: N = 21·5. $C_4H_{13}N_3,3C_6H_3O_7N_3$ requires N = 21·3 per cent.).

The *oxalate* crystallises from water, in which it is readily soluble, in flattened prisms containing $4H_2O$. After drying at 110°, it melts and effervesces at 183° (corr.) (Found: loss at 110° = 13·0. $2C_4H_{13}N_3,3C_2H_2O_4,4H_2O$ requires H_2O = 13·1 per cent. In dried substance, N = 17·5. $2C_4H_{13}N_3,3C_2H_2O_4$ requires N = 17·6 per cent.).

The *citrate* is practically insoluble in alcohol, ether, or chloroform, but readily so in water, from which it separates in well-defined, rhombic prisms containing $1H_2O$. After drying at 110°, it melts and effervesces at 206°, sintering from 200° (Found: loss at 110° = 6·3. $C_4H_{13}N_3,C_6H_8O_7,H_2O$ requires H_2O = 5·8 per cent.). In dried substance, N = 14·4. $C_4H_{13}N_3,C_6H_8O_7$ requires N = 14·2 per cent.).

The *triacetyl* derivative is practically insoluble in alcohol or light petroleum, but very readily soluble in water. It separates from 70 per cent. alcohol as a felted mass of needles, which, in contact with the solvent, change to well-defined prisms melting at 220° (corr.) (Found: N = 18·0. $C_{10}H_{19}O_3N_3$ requires N = 18·3 per cent.).

The *tribenzoyl* derivative is very sparingly soluble in ether, or light petroleum, but readily so in water or alcohol. From chloroform it separates in small, flattened prisms containing one molecule of the solvent, which is gradually lost on exposure to the air, but regained on keeping over chloroform in a desiccator. After removal of the solvent of crystallisation, it melts at 166° (corr.) (Found: $CHCl_3$ = 21·9. After forty-eight hours, this had diminished to 16·1 per cent. In dried substance, C = 71·9; H = 6·1; N = 10·1. $C_{25}H_{25}O_3N_3$ requires C = 72·2; H = 6·1; N = 10·1 per cent.).

Triethylenetetramine and its Derivatives.

Triethylenetetramine behaves very similarly to diethylenetriamine in its reactions, dissolving in water with evolution of heat, forming an insoluble carbonate when carbon dioxide is passed through its alcoholic solution, and giving precipitates with potassium mercuri-iodide, mercuric chloride, and phosphotungstic acid. It reduces silver nitrate on warming. For analysis, it was finally distilled over solid sodium hydroxide (Found: C = 48·8; H = 12·7; N = 38·0. Calc.: C = 49·3; H = 12·4; N = 38·3 per cent.).

The tetrahydrochloride separates from 70 per cent. alcohol containing excess of hydrogen chloride in minute needles (Found: Cl = 48·0. Calc.: Cl = 48·5 per cent.).

The *tetrapicrate* is very sparingly soluble, even in boiling water, from which it separates in fern-like clusters of minute, rhombic prisms melting and decomposing at 240° (corr.) (Found: N = 20·7. $C_6H_{18}N_4,4C_6H_3O_7N_3$ requires N = 21·1 per cent.).

The *hydrogen oxalate* is sparingly soluble in water, and separates in glistening needles, which effervesce at 243° (corr.) and contain $1H_2O$ (Found: loss at 110° = 3·0. $1H_2O$ requires 3·2 per cent. In dried material, C = 33·3; H = 5·5; N = 10·9. $C_6H_{18}N_4,4C_2H_2O_4$ requires C = 33·2; H = 5·2; N = 11·1 per cent.).

The tetrabenzoyl derivative dissolves sparingly in water or alcohol, but readily in chloroform. It separates from a mixture of chloroform and alcohol in fine, powdery crystals melting at 238° (corr.) (Hofmann, *Ber.*, 1890, **23**, 3717, gives 228—229°) (Found: C = 72·8; H = 6·5; N = 9·9. Calc.: C = 72·55; H = 6·1; N = 10·0 per cent.).

Methyleneaminoacetonitrile and Aminoacetonitrile.

Methyleneaminoacetonitrile was prepared substantially by the process described by Klages (*Ber.*, 1903, **36**, 1511). It was found, however, that the time of addition of the cyanide could be materially decreased without detriment to the yield so long as the temperature was maintained below 10° during the first half of the addition, and below 15° during the second. It was readily converted into aminoacetonitrile hydrochloride by shaking with the calculated quantity of *N*-alcoholic hydrogen chloride, the yield amounting to 90 per cent. of the theoretical.

Reduction of Aminoacetonitrile Hydrochloride.

With Sodium and Alcohol.—Twenty grams of the hydrochloride were added to 60 c.c. of alcohol in which 5 grams of sodium had previously been dissolved, 80 grams of sodium were added, and, after the first violent reaction had ceased, the mixture was heated on the water-bath, 250 c.c. of alcohol being gradually added. After about an hour, most of the alcohol was removed by distillation, a little 90 per cent. alcohol added to ensure that the sodium was all used, water added, and the mixture transferred to a copper flask and distilled to dryness under somewhat diminished pressure. The distillate was boiled to remove ammonia, neutralised with hydrochloric acid, and concentrated to crystallisation. The yield of ethylenediamine dihydrochloride varied from 25 to 33 per cent. of the theoretical.

With Iron and Hydrochloric Acid.—Five grams of aminoaceto-

nitrile hydrochloride were dissolved in 100 c.c. of water, 16 grams of iron filings added, and 50 c.c. of hydrochloric acid added slowly during an hour, with shaking. At the end of the reaction, the product was evaporated to dryness, distilled from a copper flask with sodium hydroxide, and the base in the distillate isolated as hydrochloride. The yield amounted to 10 per cent. of the theoretical.

With Zinc and Hydrochloric Acid.—To a solution of 6·8 grams of the hydrochloride in 100 c.c. of water, 30 grams of zinc were added, and 70 c.c. of concentrated hydrochloric acid added, as above, the product being then treated as in the previous reduction. The yield of ethylenediamine dihydrochloride amounted to 25 per cent. of the theoretical.

In conclusion, the author would thank Messrs. R. R. Baxter and J. A. Goodson for assistance in the preparation of the ethylene dichloride and ethylenediamine which formed the basis of the investigation.

WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON. [*Received, September 30th*, 1920.]

CXLVII.—*The Constitution of Carbamides. Part XIII. The Constitution of Cyanic Acid, and the Formation of Urea from the Interaction of Ammonia and Cyanic Acid at Low Temperatures.*

By EMIL ALPHONSE WERNER and WILLIAM ROBERT FEARON.

THE theory which has been put forward by one of us to explain the constitution of urea, and the mechanism of its formation from ammonium cyanate (T., 1913, **103**, 1013, 2276; 1918, **113**, 84), is based, primarily, on the conception that cyanic acid, whether in the static condition or in solution, is an equilibrium mixture, represented thus:

$$\underset{\text{Stable only at low temperature.}}{\text{(enol-form) HO·CN}} \underset{\text{Promoted by fall of t°.}}{\overset{\text{Promoted by rise of t°.}}{\rightleftharpoons}} \underset{\text{Stable at high temperature.}}{\text{HN:CO (keto-form).}}$$

Since cyanic acid is at all times very unstable, the stability referred to above is only relative. Permanent stability is only

attained by polymerisation, with the production of cyanuric acid from the keto-form and of cyamelide from the enol-form of the acid (*loc. cit.*).

Now, the ease with which ammonium cyanate is changed to urea is indicative of a close similarity in structure, and hence the constitution of cyanic acid is a question of paramount importance in solving the problem of the relation which exists between the two isomerides.

There are two reasons why previous investigators have given either little or no consideration to this important question, namely, the apparent uncertainty which has been assumed to exist as regards the nature of cyanic acid, and the general acceptance of the "carbamide" formula, which has all along masked the true relationship between urea and ammonium cyanate.

As a matter of fact, the constitution of cyanic acid is clearly indicated by (*a*) its polymerisation, and (*b*) its hydrolysis and behaviour towards ammonia at low temperatures.

(a) *Polymerisation of Cyanic Acid.*

Senier and Walsh (T., 1902, **81**, 290) showed that the spontaneous polymerisation of cyanic acid yielded a product which contained, in round numbers, 70 per cent. of cyanuric acid and 30 per cent. of cyamelide. This was the result of a single experiment, in which no particular effort was made to control the temperature at which polymerisation took effect.

If the theory of the polymerisation of cyanic acid which was propounded by one of us is sound (T., 1913, **103**, 1016),* and if cyanic acid is an equilibrium mixture, as indicated above, it follows that its composition at any particular temperature will be revealed by the relative proportions of the two polymerides formed. This inference, which was predicted when the theory was put forward, has now been verified by analyses of the products formed when liquid cyanic acid polymerised at different temperatures.

At zero the acid was stable for about four hours, provided it was not agitated, and it polymerised slowly. In order to obtain a reasonable control of the temperature at which polymerisation took place, only very small quantities of the acid were dealt with in each experiment (see experimental part).

The results were as follows:

* For the sake of brevity, the theory is not reproduced here; in order to appreciate the significance of the results obtained it is necessary to consult the paper on the mechanism of the polymerisation of cyanic acid to which reference is made.

TABLE I.

Temperature of polymerisation (approximate).	Weight of polymeride.	Cyanuric acid found.	Percentage composition of polymeride.	
			Cyamelide.	Cyanuric acid.
0°	0·53 gram.	0·216 gram	59·25	40·75
5	0·42 „	0·174 „	58·58	41·42
10	0·105 „	0·045 „	57·27	42·73
20	0·24 „	0·136 „	42·92	57·08

In several experiments, where the acid polymerised when the containing vessel was plunged into water at 20°, the temperature rose suddenly to about 70°, and the proportions of cyanuric acid formed were from 70 to 80 per cent. Since the latter acid is almost the sole product found when polymerisation takes place at high temperatures, as, for example, when urea is heated above its melting point (132°) (T., 1913, **103**, 2276), it follows that, under such conditions, cyanic acid is liberated in the keto-form. Liquid cyanic acid, on the other hand, must be an equilibrium mixture, the composition of which is a function of the temperature; thus, at 0°, it may be represented as approximately

$$\underset{\text{60 per cent.}}{\text{HO·CN}} \rightleftharpoons \underset{\text{40 per cent.}}{\text{HN:CO}}$$

(b) *Hydrolysis of Cyanic Acid, and its Reaction with Ammonia at Low Temperatures.*

Whenever urea is formed in a reaction where cyanic acid and ammonia are concerned, it has always been assumed that it must originate from the transformation of ammonium cyanate produced in the first instance. Since the difference between the two isomerides is nothing more than that of the products of the union of ammonia with the enol- and keto-forms, respectively, of cyanic acid, it is obvious that the above assumption is superfluous.

A quantitative study of the hydrolysis of cyanic acid has supplied convincing evidence that both isomerides are simultaneously formed when ammonia reacts with the acid at low temperatures. Not less than six consecutive changes are involved during the progress of this reaction, and these are conveniently divided into two groups, as follows:

Primary changes:

(1) $(\text{HOCN} \rightleftharpoons \text{HNCO}) + \text{H}_2\text{O} = \text{CO}_2 + \text{NH}_3$.

(2) $\text{HOCN} + \text{NH}_3 = \text{NH}_4\cdot\text{OCN}$.

(3) $\text{HN:CO} + \text{NH}_3 = \text{HN:C}\begin{matrix}\text{NH}_2\\ \vert \\ \text{O}\end{matrix}$.

Secondary changes:

(4) $NH_3 + CO_2 + H_2O = NH_4HCO_3$.
(5) Formation of biuret from interaction of urea and HNCO.
(6) Production of cyamelide.

The main question was to prove the validity of reaction (3). This was successfully accomplished when an approximately $N/4$-solution of cyanic acid was allowed to hydrolyse at 0°. Under such conditions, the secondary changes were almost completely suppressed up to the point at which the primary changes were completed. A solution of cyanic acid was prepared by the addition of the theoretical amount (62·5 c.c.) of N-nitric acid to 5·05 grams of pure potassium cyanate dissolved in 187·5 c.c. of water. The solution (250 c.c.) was prepared at 0°, and maintained at this point during all the analyses.

The following results were obtained with 25 c.c., taken at intervals of fifteen minutes (Expt. II).

TABLE II.

Time in minutes.	Cyanic acid present (free, and as NH_4OCN). Gram.	Urea formed (theoretical). Gram.		Urea found. Gram.
—	0·230*	—		—
15	0·195	0·024		0·018
30	0·165	0·045	Total urea	0·038
45	0·129	0·070	at this stage	0·063
60	0·109	0·084	=0·313.	0·081
75	0·101	0·090		0·087
90	0·094	0·094		0·089
1230	0·061	0·118		not estimated.

* 0·267 Gram is the theoretical amount, from the weight of potassium cyanate taken. The deficiency found at the outset was due to: (*a*) loss by volatilisation—the solution had a very pungent odour; (*b*) time elapsed during addition of nitric acid, and impossibility of avoiding to a small extent the change $HOCN + H_2O + HNO_3 = NH_4NO_3 + CO_2$.

The theoretical values for urea formed were calculated from the amounts of cyanic acid which had disappeared after each interval on the basis $2HNCO \longrightarrow CON_2H_4$.

It will be seen that, under the conditions stated, the hydrolysis of cyanic acid was comparatively slow; thus, about ninety minutes were required before all free acid had disappeared. At this stage the three primary reactions had been completed, hence there was no object in estimating urea formed beyond this point, since it could only then arise from the slow transformation of ammonium cyanate, as a result of its hydrolytic dissociation, thus:

$$NH_4OCN = NH_3 + HOCN \rightleftharpoons HNCO.$$

This is strikingly shown by the last result, where, in the interval between 90 and 1230 minutes, only 0·033 gram of cyanic acid (as ammonium cyanate) had been removed, and when this is considered in connexion with the fact that in 75 minutes from the commencement of the change 0·313 gram of urea was formed, there can be no doubt that the latter can only have been produced as the direct result of reaction (3). Now, after 75 minutes, when the disturbing effects of reaction (4) were just noticeable,* half of the solution (125 c.c.) had been used, that is, 1·15 grams of cyanic acid, capable of yielding 0·8 gram of either urea or ammonium cyanate, had taken part in the completion of reactions (1), (2), and (3). Hence (0·8—0·313) 0·487 gram of ammonium cyanate was formed, which shows that cyanic acid, in aqueous solution at 0°, had reacted with ammonia as a mixture of HOCN = 60·9 per cent. and of HNCO = 39·1 per cent., a result almost identical with that arrived at from the study of the polymerisation of the anhydrous acid at the same temperature.

As regards the secondary changes, the production of biuret confirms reaction (3), since it must be a sequence of it (compare Werner, T., *loc. cit.*; P., 1914, **30**, 262), and whilst its formation does not affect the above result as regards the proportion of cyanic acid which reacted as HN:CO, its presence was mainly responsible for the low values found for urea formed in the early stages of the reaction. In agreement with theory, the formation of biuret was largely confined to this period.

The production of a trace of cyamelide in these experiments proves that cyanic acid was liberated in the enol-form, since the generation of this polymeride takes effect from the change HOCN $\longrightarrow$ HNCO. When a solution of ammonia in pure ether at $-8°$ was gradually added to a similar solution of cyanic acid, the crystalline product which immediately separated was found to be a mixture of ammonium cyanate and urea in the proportion of 6 to 2·6 respectively.

Note on the Xanthhydrol Test for Urea.

The use of xanthhydrol for the detection and estimation of urea depends on the formation of a very sparingly soluble condensation product. Fosse (*Compt. rend.*, 1907, **145**, 813; 1913, **156**, 1938) recommends pure acetic acid as the solvent in applying the test. This introduces certain limitations, and where the detection of a

* For this reason, 75 minutes must be taken as the limit up to which the change had proceeded undisturbed in accordance with the primary reactions.

trace of urea in a relatively large volume of water is desired, the process is tedious.

As a matter of fact, xanthhydrol is not a test for "free" urea; thus, in alcoholic solution, no reaction was effected, even after heating at 100° in a sealed tube for several days. After the addition of one drop of concentrated hydrochloric acid, the condensation product was precipitated, and its formation was completed within ten minutes. The solubility of dixanthylurea in pure alcohol at 15° was equal to 0·009 gram in 100 c.c.

A salt of urea must be formed in order to bring about the necessary configuration of the urea molecule before it can react with xanthhydrol, and, in accordance with this view, the test can be applied as follows.

A saturated aqueous solution of xanthhydrol (containing 0·13 gram in 1000 c.c. at 15°) is readily prepared by adding the reagent, previously dissolved in 2 c.c. of alcohol, to a litre of boiling water. The cold solution (filtered, if necessary), when added in considerable excess (not less than 6 vols. to 1) to an aqueous solution containing urea to which a few drops of hydrochloric acid have been added, will reveal 1 part in 10,000 within fifteen seconds, whilst 1 part of urea in 800,000 can be detected in about ten minutes.

The solution of xanthhydrol loses its sensitiveness after about a week, on account of gradual oxidation to xanthone.

Experimental.

I. *Polymerisation of Cyanic Acid.*—The results given in table I were obtained as follows: cyanic acid was prepared from pure, dry cyanuric acid, which was heated electrically in a hard glass tube so arranged that the heating could be continued right up to the neck of the receiver. The construction of the latter was such that liquid cyanic acid collected in the narrow space between an inner and an outer vessel, each of which was kept at 0°. A relatively large surface of the acid was thus maintained at a constant temperature, and by careful avoidance of agitation, which was found to be a great promoter of the change, polymerisation was allowed to proceed as slowly as possible. The ice in the outer vessel only was displaced by water at the temperature at which it was desired to bring about polymerisation; in this way only was it possible to control, within reasonable limits, the temperature at which the change took effect.

A weighed quantity of the polymeride was extracted with hot water; the cyanuric acid present was estimated by titration with *N*/10-sodium hydroxide, using phenolphthalein as indicator.

Whilst it was necessary to prepare small portions of cyanic acid for each experiment, the values given represent the mean of many more experiments than are recorded.

II. *Formation of Urea at* 0°.—Cyanic acid was estimated by precipitation with an excess of silver nitrate, and the silver cyanate, dissolved in dilute nitric acid, was titrated by Volhard's method. The filtrate, freed from the excess of silver, was rendered just alkaline by addition of pure lime, and, after the removal of all traces of ammonia, urea was estimated in the residue by (*a*) the "hypobromite" method, (*b*) decomposition by urease, and (*c*) precipitation with xanthhydrol. The presence of biuret was proved by the copper test.

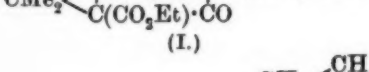
Part of the expense of this research was defrayed by the Mackinnon Research Studentship of the Royal Society granted to one of us (W.R.F.).

UNIVERSITY CHEMICAL LABORATORY,
TRINITY COLLEGE, DUBLIN. [*Received, September 22nd,* 1920.]

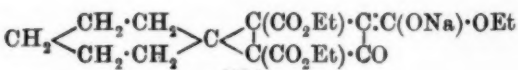
CXLVIII.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. Part I. Some Derivatives of* cyclo*Pentene and* dicyclo*Pentane.*

By ERNEST HAROLD FARMER and CHRISTOPHER KELK INGOLD.

PERKIN and Thorpe (T., 1901, **79**, 729) showed that when ethyl *αα'*-dibromo-*ββ*-dimethylglutarate is condensed with ethyl malonate in the presence of an excess of sodium ethoxide there is formed a remarkable yellow sodium compound, to which hitherto the formula I has been ascribed. Numerous derivatives of this substance were prepared both by hydrolysis and by alkylation and subsequent hydrolysis, and many of the products so obtained were subjected to oxidation and reduction. Much more recently, one of us, in conjunction with Prof. J. F. Thorpe, prepared from ethyl *αα'*-dibromo*cyclo*hexane-1:1-diacetate a second, rather similar yellow sodium compound (II). This also yielded a large number



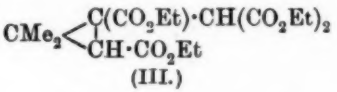
(I.)



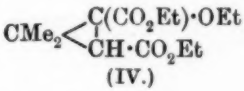
(II.)

of hydrolytic products analogous, broadly speaking, to those of the *gem*-dimethyl series, but exhibiting a number of very striking differences, which were studied in some detail (T., 1919, **115**, 320) and correlated in a definite manner to the constitutions of the substances concerned.

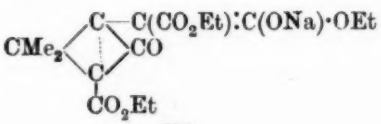
In the course of neither of these investigations has there been discovered any fact which could reasonably be regarded as casting doubt on the bridged structures assigned to these sodium compounds and to their more immediate derivatives. On the contrary, much evidence confirming these structures has been accumulated. The principal item consists, of course, in the mode of formation of the sodium compounds. Thus, when ethyl $\alpha\alpha'$-dibromo-$\beta\beta$-dimethylglutarate is treated with two molecular proportions of ethyl sodiomalonate, there is formed the sodium compound of an ester, which, as it can readily be alkylated, cannot but have the structure III. This structure is quite inevitable, and is strictly analogous to that of ethyl ethoxycaronate (IV), which is formed by the action of sodium ethoxide on the dibromo-ester. The ester (III), on being treated with sodium in xylene, or with an excess of alcoholic sodium ethoxide, loses one molecule of ethyl alcohol, and is converted into the yellow sodium compound, which therefore must have either formula I or formula V. Of these, the former alone is capable of



(III.)



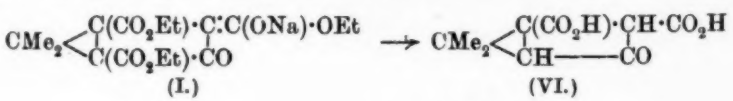
(IV.)



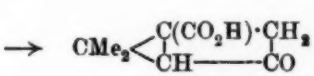
(V.)

interpreting the many decompositions of the substance.

Quite recently, doubt has been cast by Toivonen (*Annalen*, 1919, **419**, 176) on the bridged constitution which has hitherto been assigned to these compounds. When the sodium compound (I) is hydrolysed by acids, it yields, first, a dibasic acid (VI), and, finally, a monobasic acid (VII). This monobasic acid was obtained by

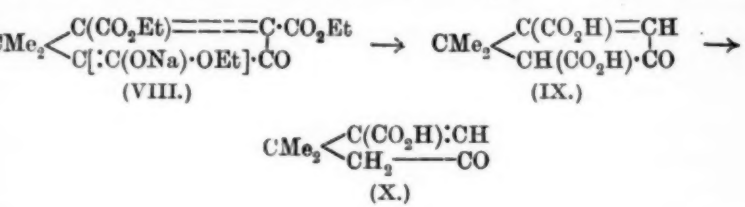


(I.) (VI.)



(VII.)

Toivonen in the course of some experiments on the oxidation of *iso*dehydrofenchoic acid, and, as a result of his investigations, he formed the opinion that, not only this acid, but all the compounds of the series, including the yellow sodium compound itself, were unsaturated substances containing the *cyclo*pentene, and not the *dicyclo*pentane, ring system. Thus, according to Toivonen, the sodium compound would be represented by the formula VIII, the dibasic acid by IX, and the monobasic acid by X. Toivonen found

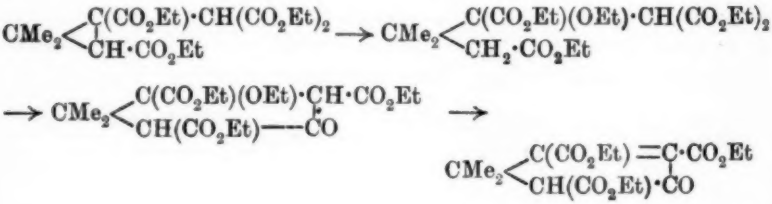


(VIII.) (IX.) (X.)

that the oxidation of *iso*dehydrofenchoic acid by alkaline permanganate proceeded in two stages. In the first place, a diketonic acid (XI) was produced. This then underwent internal condensation under the influence of the alkali, and gave Perkin and Thorpe's acid, with the elimination of one molecule of water. Toivonen represents this reaction as follows:

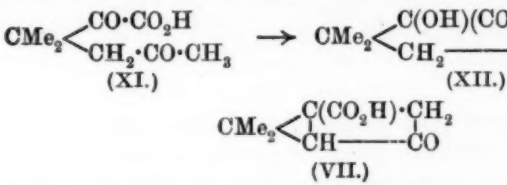
(XI.) (X.)

We therefore have two methods of formation of one and the same substance which are exceedingly difficult to reconcile with one another. In fact, one must either assume that the conversion of the ester (III) into the yellow sodium compound, instead of being a simple Dieckmann condensation, is a remarkable change involving the rupture by alcoholysis of the *cyclo*propane ring, possibly as in the following scheme:



or regard the internal condensation of dimethyldiketohexoic acid (XI) as taking place in two stages. In the first place, there must

be formed a cyclic aldol condensation product (XII), which is then dehydrated across the *cyclo*pentane ring:

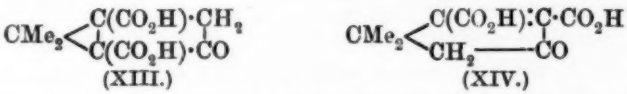


(XI.) (XII.) (VII.)

Both alternatives appear almost equally extraordinary.

The subject therefore obviously required fresh investigation, and some months ago we were asked by Prof. J. F. Thorpe to undertake this work, and there have now been obtained results which show unquestionably that, for the series of compounds with which we are here concerned, the bridged, and not the unsaturated, constitution is correct.

Turning, first, to the facts which have already been placed on record, one observes two reasons why the formulæ suggested by Toivonen cannot be regarded as adequate. The first concerns the dibasic acid, the bridged formula for which is VI, the double-bonded formula IX. That the alternative formulæ, XIII and

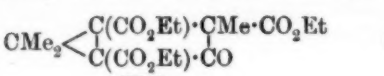


(XIII.) (XIV.)

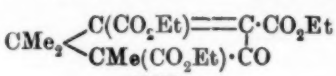
XIV, are incorrect is proved by the fact that the acid is a tautomeric substance; it readily gives a coloration with ferric chloride, and its ester can be alkylated. Now an acid of the formula IX, in which, as an examination of structural models shows, the carboxyl groups are actually further apart than is the case with such compounds as *trans*-hexahydro*iso*phthalic acid or *cis*-hexahydroterephthalic acid, would not be expected to form an anhydride. Actually, however, the acid does form an anhydride with the greatest of ease, a fact which is in full accordance with the bridged-ring formula (VI).

The second point arises in connexion with the ester produced by methylating the yellow sodium compound with methyl iodide. The bridged and unsaturated structures for this substance are shown in formulæ XV and XVI. On treating with alcoholic potassium hydroxide, there is formed the lactone of a hydroxytribasic acid, the production of which involves (*a*) the hydrolysis of all three carbethoxyl groups to carboxyl; (*b*) the loss of one carboxyl group by elimination of carbon dioxide; (*c*) fission, with the addition of water in the immediate neighbourhood of the

ketone group, which thus becomes a carboxyl group; (*d*) a further fission, with the addition of water. Now, whether formula XV

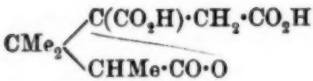


(XV.)

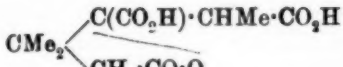


(XVI.)

or formula XVI is adopted, process (*a*) can only take place in one way, process (*b*) in two ways, and process (*c*) in two ways. If one adopts the structure XV, the addition of a further molecule of water, process (*d*), must involve the fission of one of the *cyclo*-propane bonds. This could take place in six ways. On the other hand, if formula XVI be accepted, the addition must take place at the double bond, since the product is fully saturated. This might occur in two ways. On considering the combinations of these possibilities, one observes that, as many lead to the same formulæ, there are but six possible structures for such a hydroxy-tribasic acid derived from an ester of the constitution XV, and six from an unsaturated ester of the constitution XVI. The properties of the lactone (*loc. cit.*) show, however, that in the corresponding hydroxy-acid, (*a*) the hydroxyl group is in the γ-position with respect to one of the three carboxyl groups; (*b*) that no two carboxyl groups are attached to the same carbon atom; (*c*) that the two carboxyl groups, other than that to which the hydroxyl group is in the γ-position, are attached to two carbon atoms directly united. These conditions reduce the number of possible formulæ derived from the structure XV to three, one of which is the accepted one, and the number from XVI to one only, namely, XVII. It will be seen that this differs from the customary formula



(XVII.)

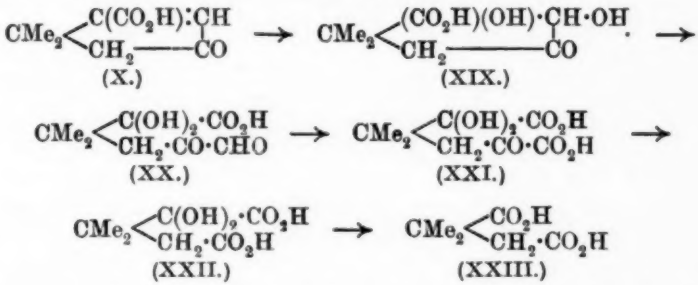


(XVIII.)

(XVIII) only in the position of the single methyl group. The difference, however, is an important one, as the lactonic acid was found to exist in two forms, namely, a *cis*- and a *trans*-form (or meso- and racemic), each of which yields its own anhydride, that of the *trans*-lactonic acid passing on distillation into that of the *cis*-lactonic acid. This property is characteristic of substances of the type of *s*-dimethylsuccinic acid, and clearly proves that there exists in the molecule of the lactonic acid a free, open-chain succinic acid residue in which both the carboxyl-bearing carbon atoms are asymmetric. This condition is fulfilled by formula XVIII, but formula XVII is obviously incorrect, as it lacks one of the necessary asymmetric carbon atoms in the succinic acid group. One must

therefore conclude that the unsaturated structure XVI for the methylation product of the yellow sodium compound is incapable of interpreting the properties of the products obtained by hydrolysis.

Toivonen, however, was more deeply impressed with the behaviour of the monobasic acid on oxidation. Perkin and Thorpe had shown (*loc. cit.*) that, when treated with alkaline permanganate, it was converted into *αα*-dihydroxy-*ββ*-dimethylglutaric acid (XXII). Toivonen proved that the reaction could be carried out at the ordinary temperatures, and, as it is capable of being easily explained along conventional lines if the unsaturated structure be assumed, he saw in it conclusive confirmation of this method of formulation. The successive stages are as follows:



In practice, between four and five atoms of oxygen are taken up, and the product is a mixture of dihydroxydimethylglutaric acid (XXII) and *as*-dimethylsuccinic acid (XXIII).

In spite of the apparent simplicity of this explanation, the issue is not, in reality, quite so clear. For, as was shown in the paper by Ingold and Thorpe (*loc. cit.*), the bridge-bond in such *dicyclo*-pentane systems is in a condition of great strain, and may become —in fact, in certain circumstances it undoubtedly does become—the most unstable part of the molecule, giving rise to reactions the similarity of which with the reactions characteristic of unsaturated compounds is very striking. This state of strain owes its origin to the fact that, in both the rings to which the bridge-bond is common, the internal angles are considerably less than the normal angle at which two free valencies are inclined (Ingold and Thorpe, *loc. cit.*). The case of carone is very different. Here the internal angles between the valencies in the two rings separated by the bridge differ in opposite ways from the normal angle of inclination of carbon valencies. There is, therefore, a mutual accommodation existing between the strains which react on the carbon atoms terminating the bridge, rendering the latter stable to a considerable degree. The theory of the matter may readily be placed on

a quantitative basis by a simple calculation on lines indicated elsewhere (*loc. cit.*; note, this vol., p. 603). Therefore Toivonen's argument that, because carone, dimethyl*dicyclo*heptanone (XXXI, p. 1370), can be oxidised by permanganate to a *cyclo*propane derivative, namely, caronic acid (XXXII, p. 1370), the acids derived from dimethyl*dicyclo*pentanone should behave similarly with this reagent, cannot be regarded as being in the least degree convincing. On a priori grounds, it might be very difficult to discover an oxidising agent capable of attacking the four-membered ring at the carbonyl group, and yet leaving the somewhat unstable bridge-bond intact. On the other hand, should such a substance as caronic acid be obtainable by oxidation under special and carefully regulated conditions, the circumstance could not but be regarded as the clearest possible proof of the dicyclic constitution of this series of compounds. This proof we have now been able to supply.

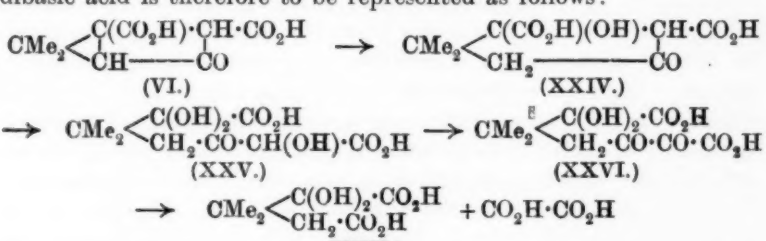
The general plan pursued in our experiments was as follows. If the alternative formulæ VI and IX for the dibasic acid, and the two formulæ XV and XVI for the methylation product of the yellow sodium compound, be examined, it will be noticed that in the one case a carboxyl group, and in the other a methyl group, is in a different position relative to the *gem*-dimethyl group in the two alternative formulæ. It should be possible to ascertain the true positions of these groups by oxidation. Thus, for example, whilst the ester (XV), after hydrolysis and oxidation, might perhaps yield some derivative of $\beta\beta$-dimethylglutaric acid, an ester the formula of which is XVI should give derivatives, not of $\beta\beta$-dimethylglutaric acid, but of $\alpha\beta\beta$-trimethylglutaric acid. There are similar differences in the oxidation products to be expected from dibasic acids having the structures VI and IX. A number of interesting results have already been obtained in this field, but it has become apparent that an extended investigation is necessary both in the series with which we are here concerned and in other related ones. It is therefore our desire to place on record at the present time only a limited number of experiments on the oxidation of the dibasic acid (VI), which, however, supply singularly convincing evidence regarding its structure.

In the first place, when an aqueous solution of the dibasic acid is titrated with cold alkaline permanganate, a sharp end-point is reached after three atoms of available oxygen have been taken up. The resulting solution contains $\alpha\alpha$-dihydroxy-$\beta\beta$-dimethylglutaric acid and oxalic acid, the reaction

$$C_9H_{10}O_5 + 3O + 2H_2O = C_7H_{12}O_6 + C_2H_2O_4$$

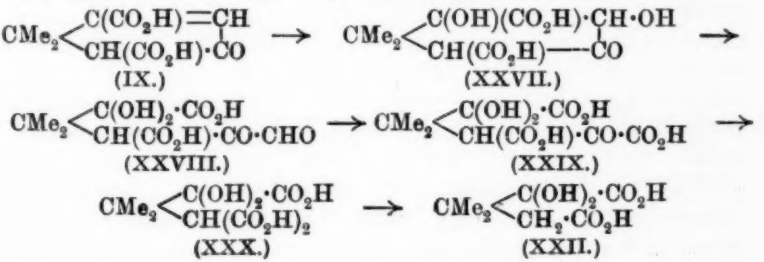
being apparently quantitative. The behaviour of the dibasic acid

with permanganate is therefore very similar to that of the monobasic acid (VII). The remarkable fact regarding the production of this dihydroxydimethylglutaric acid by the action of cold alkaline permanganate on these acids is that the fission of the bridge-bond is not due to oxidation, but is of a purely hydrolytic character. There is therefore no analogy to fission of the double bond in unsaturated substances by permanganate, the first stage of which involves the addition of two hydroxyl groups. The fission of the bridge must be assumed to be due to the addition, not of 2OH, but of H·OH, otherwise it is not possible to account for the structure of the product. The oxidation, for example, of the dibasic acid is therefore to be represented as follows:



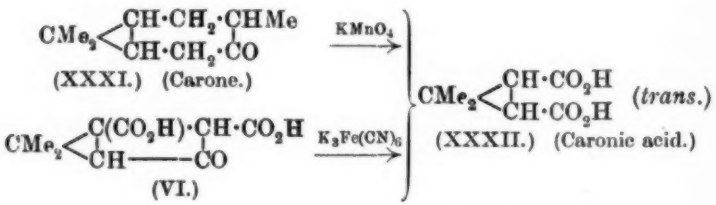
If the process is conducted with care, no dimethylsuccinic acid is formed. A precisely analogous scheme, involving an intermediate hydrolytic product similar to XXIV, and two intermediate oxidation products, like XXV and XXVI, may be considered as representing the course of the oxidation of the monobasic acid—only in this case four atoms of oxygen are taken up, as the final product, which replaces oxalic acid in the scheme outlined above, is not formic acid, but carbon dioxide.

The formation of oxalic acid along with dihydroxydimethylglutaric acid when the dibasic acid is oxidised affords an interesting confirmation of the existence originally of the bridged structure. For, if the double-bonded formula IX for the original acid were correct, the production of oxalic acid as a main product would be impossible. Four, and not three, atoms of oxygen would be taken up, the successive changes being represented as follows:



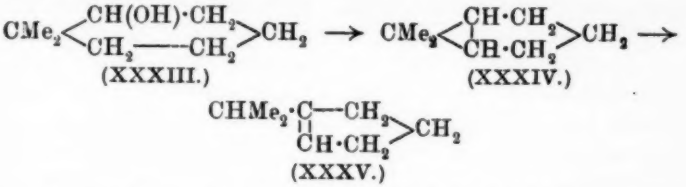
In this method of representation, the intermediate products XXVII to XXX are strictly analogous to the substances XIX to XXII which figure in the corresponding scheme (p. 1367) for the oxidation of the monobasic acid, whilst the direct elimination of a carboxyl group as carbon dioxide from the acid XXX appears to be the only method of accounting for the unsubstituted methylene group in the final product. We are unable to see any plausible alternative mechanism whereby the formation of oxalic acid along with dihydroxydimethylglutaric acid by the oxidation of an unsaturated substance having the formula IX might be explained.

Owing to the curious hydrolytic action on the bridge-bond to which reference has just been made, it does not appear possible to obtain *cyclo*propane derivatives by oxidation with permanganate. We have experimented with many other oxidising agents under a variety of conditions, and have discovered two reagents by means of which it is possible to produce caronic acid from the dibasic acid, which therefore must have the bridged structure VI. These are hydrogen peroxide and potassium ferricyanide. In the former case, the conditions necessary in order to obtain a good yield of caronic acid appear rather difficult to determine, but with cold ferricyanide the oxidation proceeds very smoothly, and, if a little of the reagent is added each day, is complete in rather more than a week, when an excellent yield of *trans*-caronic acid can be extracted from the solution. The direct comparison with the case of carone asked for by Toivonen now becomes possible:



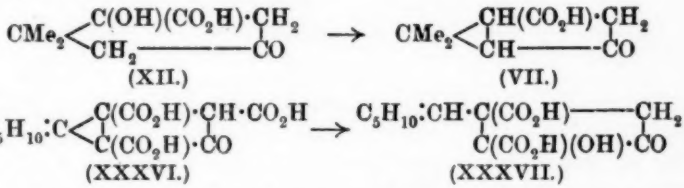
If this experiment places, as we believe it does, the bridged constitution beyond doubt, there appears to be no alternative to accepting the mechanism proposed on p. 1365 for the internal condensation of Toivonen's dimethyldiketohexoic acid (XI). Such a reaction is not, however, entirely without precedent, for the intermediate aldol-condensation product (XII) is a cyclic pinacoline alcohol very similar in constitution to the dimethyl*cyclo*hexanol (XXXIII), the dehydration of which has been investigated by Meerwein (*Annalen*, 1914, **405**, 129), who found it to take place across the ring, the final product being *iso*propyl*cyclo*-

pentene (XXXV). We assume that intermediately a bridged compound (XXXIV) is formed:



(XXXIII.) (XXXIV.) (XXXV.)

The difference between this case and that with which we are concerned lies in the fact that the hydroxy-compound (XII), owing presumably to the presence of the ketone and carboxyl groups, undergoes dehydration spontaneously, or at any rate under very mild conditions. For the same reason, the reaction stops at the first stage: the presence of the carboxyl group makes the analogous isomerisation impossible. Although no reaction resembling this isomeric change has been observed amongst the derivatives of *gem*-dimethyl*dicyclo*pentane, there has been noticed (Ingold and Thorpe, *loc. cit.*) in the *cyclo*hexane*spirodicyclo*pentane series a hydrolytic decomposition showing a considerable degree of similarity. The connexion is best exhibited by means of the formulæ expressed below, and from these it will be seen that both stages of the above scheme for the dehydration of dimethyl*cyclo*hexanol have their counterpart. The *cyclo*hexyl*cyclo*butanolone acid (XXXVII) is obviously incapable of eliminating the elements of water and passing into a *cyclo*butene derivative as the strict analogy requires.



(XII.) (VII.) (XXXVI.) (XXXVII.)

The above considerations have an obvious implication regarding the internal condensation of other diketones, and it is hoped in the future to devote attention to this and similar questions.

Experimental.

*Oxidation of Dimethyl*dicyclo*pentanonedicarboxylic Acid* (VI, p. 1363) *by Cold Alkaline Permanganate: Formation of αα-Dihydroxy-ββ-dimethylglutaric Acid and Oxalic Acid.*

Two grams of the *dicyclo*pentanone acid were dissolved in a small excess of aqueous potassium carbonate and carefully titrated

in the cold with a 3 per cent. solution of potassium permanganate. When three atoms of oxygen had been taken up, the permanganate ceased to be decolorised. The solution was then treated with a current of steam and filtered, the precipitate of manganese dioxide being extracted with boiling water. The combined filtrates were acidified with hydrochloric acid, boiled for a few minutes, and then rendered alkaline with ammonia. On adding calcium chloride to this solution, there was obtained a precipitate of calcium oxalate, which was collected and washed with dilute acetic acid in order to remove any traces of admixed calcium carbonate. The filtrate from the calcium oxalate was evaporated to a small bulk, acidified with hydrochloric acid, and exhaustively extracted with pure ether. On drying and evaporating the extract, there was obtained a nearly quantitative yield of $\alpha\alpha$-dihydroxy-$\beta\beta$-dimethylglutaric acid. The acid prepared in this way melted at 83—84°, and after recrystallisation from chloroform at 84° (Found: C = 44·20; H = 6·37. Calc.: C = 43·7; H = 6·3 per cent.).

Further proof of the identity of the acid was obtained by means of a direct comparison with a specimen prepared from the hydrogen ester of $\alpha\alpha$-dibromo-$\beta\beta$-dimethylglutaric acid (Perkin and Thorpe, *loc. cit.*, p. 757). Both preparations, as well as a mixture of the two, melted at 84°.

$\alpha\alpha$-Dihydroxy-$\beta\beta$-dimethylglutaric acid may also be obtained from the *dicyclo*pentanone acid by oxidation with sodium manganate.

*Oxidation of Dimethyl*dicyclo*pentanonedicarboxylic Acid* (VI, p. 1363) *by Cold Ferricyanide: Formation of* trans-*Caronic Acid.*

Thirty-three grams of potassium ferricyanide and 8 grams of potassium carbonate were dissolved in 140 c.c. of water, and one-fifth of this solution was added daily to 2 grams of the *dicyclo*pentanone acid dissolved in a slight excess of aqueous potassium carbonate. After the addition of the reagent was finished, the mixture was allowed to remain for another period of five days, and was then acidified and extracted repeatedly with pure ether. On drying and evaporating the ether, there remained a crystalline residue, which, after washing with chloroform and recrystallising from water, melted at 213° [Found: C = 53·13; H = 6·41. Calc.: C = 53·1; H = 6·4 per cent. 0·0435 required 40·7 c.c. of 0·0135*N*-$Br(OH)_2$. $C_5H_8(CO_2H)_2$ requires 40·8 c.c.].

There can be no doubt that this substance is *trans*-caronic acid. It was identified with a known specimen of this acid by direct

comparison and by the method of mixed melting point. In addition, it was converted by means of hydrobromic acid and by hydrochloric acid into terebic acid, which was similarry identified by comparison with a known specimen and by a mixed melting-point determination. Before we were aware that the product of this oxidation was *trans*-caronic acid, we recrystallised the crude residue from the ether from concentrated hydrochloric acid. This treatment caused a considerable degree of conversion into terebic acid. Consequently, after several recrystallisations we obtained pure terebic acid apparently as the sole crystalline oxidation product. The extraordinary ease with which this reaction takes place does not appear to have been noticed previously (compare Beasley, Ingold, and Thorpe, T., 1915, **107**, 1080).

A search for *cis*-caronic acid amongst the residues of the oxidation proved fruitless.

trans-Caronic acid may also be obtained by oxidising the original acid with cold alkaline hydrogen peroxide.

We have to thank the Chemical Society for a Research Grant which has defrayed a considerable portion of the cost of this investigation.

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CXLIX.—*A New Type of Compound containing Arsenic.*

By GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER.

HITHERTO, our knowledge of additive compounds formed from arsines has been restricted to those of the cacodyl series, and the compounds in question are of the co-ordination type and contain such elements as platinum, mercury, and copper. The authors have found that many arsines of the type $R_1R_2R_3As$, where R_1, R_2, and R_3 may be similar or dissimilar alkyl or aryl groups, combine readily with methyldi-iodoarsine and with the corresponding ethyl and phenyl derivatives to give brightly-coloured substances varying in shade from pale yellow to deep orange, and of the general type $R_1R_2R_3As,RAsI_2$. They are completely dissociated into their parent substances on dissolving in benzene, but evaporation of such solutions gives the pure additive compound

once more. They react in benzene solution with methyl iodide, with precipitation of the methiodide of the arsine, the alkyl- or aryl-di-iodoarsine remaining in solution. The solid additive compounds cannot be said to be unstable, remaining unchanged indefinitely under ordinary conditions, but they crystallise only with difficulty from some solvents, apparently owing to the retarding influence of the latter on the rate of addition of the two substances, giving rise to the additive compound.

The authors hesitate, without further experimental work, to suggest definite formulæ for the additive compounds. These may evidently be simple "molecular compounds" or compounds analogous to those formed between arsines and methylene iodide, and of the type $R_1R_2R_3IAs{\cdot}AsRI$.

In support of this structure can be cited the fact that, as a rule, an additive compound is paler than the di-iodoarsine from which it is formed, and the further fact that iodine attached to arsenic in the quinquevalent condition has no chromophoric properties. Against the structure given above, however, is the fact of ready dissociation in benzene solution.

Phenyldimethylarsine, phenylmethylethylarsine, and phenyldiethylarsine, in their behaviour towards di-iodoarsines, illustrate well the subject under discussion, and the melting points of the various substances involved are tabulated below:

	$MeAsI_2$ (30°).	$PhAsI_2$ (15°).	EtAsI (−9°).
$PhMe_2As$ (liquid)	94°	69°	44°
PhMeEtAs (liquid)	84	55°	—
$PhEt_2As$ (liquid)	79	—	—

In each of the nine cases allowed for by this table, combination undoubtedly occurred, since, on mixing the pair of substances in question, heat was evolved. Only six compounds were actually isolated, and from the melting-point regularities this fact can no doubt be attributed to the low melting points of the three compounds which could not be isolated. Attention should perhaps be drawn to the isomerism of the additive compounds

$$PhMeEtAs,MeAsI_2 \text{ and } PhMe_2As,EtAsI_2.$$

On the other hand, certain arsines show no tendency to form additive compounds with di-iodoarsines, no heat being evolved on mixing the substances in question. Thus, diphenylmethylarsine, triphenylarsine, and other aromatic arsines could not be caused to combine with di-iodoarsines under a wide range of experimental conditions.

Phenyldichloroarsine has also been found to form an additive compound with the most reactive of the arsines in our possession,

namely, phenyldimethylarsine. The compound is strictly analogous to the iodo-compounds just described, and the effect of heat on chloro-additive compounds generally, if they can be prepared, will be investigated, since some light might thus be thrown on the interaction between, say, triphenylarsine and arsenious chloride, which proceeds in a very irregular manner and is greatly influenced by temperature (compare Michaelis and Loesner, *Ber.*, 1891, **27**, 294, etc.).

The iodo-derivatives of arsenic have been found to be the most suitable for the preparation of the various types of arsines. They react almost quantitatively with Grignard reagents, giving the expected arsines in all cases so far studied. The use of arsenious chloride or bromide (Auger and Billy, *Compt. rend.*, 1904, **139**, 597; Hibbert, *Ber.*, 1906, **39**, 160) is to be avoided, as very low temperatures are necessarily involved.

Experimental.

Methyldi-iodoarsine.

This substance was prepared by Auger's method (*Compt. rend.*, 1906, **142**, 1151), and was purified by distillation under diminished pressure. It boiled without decomposition at 128°/16 mm., and gave, on cooling, a bright yellow solid melting at 30° (Auger, *loc. cit.*, gives 25°). On one occasion, 320 grams of arsenious oxide, converted into sodium methylarsinate by the method described by Klinger and Kreutz (*Annalen*, 1888, **249**, 149), gave more than 500 grams of pure, redistilled methyldi-iodoarsine (Found: M.W. [by cryoscopic method in benzene]=331, 340. Calc.: M.W.=344).

In view of certain results obtained in other directions, it is considered possible that in other solvents methyldi-iodoarsine may be associated, although at present no direct evidence can be put forward in connexion with this point. The ease with which methyldi-iodoarsine may be prepared renders this substance a very convenient starting material for the preparation of arsenic derivatives. In this connexion, it is of interest to note that whereas methyl iodide reacts almost quantitatively in the course of a few hours with sodium arsenite in aqueous-alcoholic solution, ethyl iodide reacts much more slowly, a 57 per cent. conversion of sodium arsenite into ethyldi-iodoarsine (see below) being the maximum so far obtained.

Ethyldi-iodoarsine.

The product obtained (compare McKenzie and Wood, this vol., p. 408) by the reduction of ethylarsinic acid was dried over

calcium chloride, and the sulphur dioxide present removed by gentle warming under diminished pressure, the whole of the liquid finally being distilled under the same conditions. Ethyldi-iodoarsine was obtained in this way as a reddish-yellow oil boiling at 126°/11 mm., and setting to a pale yellow, crystalline solid (m. p. −9°) on cooling in solid carbon dioxide.

Phenyldi-iodoarsine.

A mixture of phenyldichloroarsine (34 grams), 90 grams (a large excess) of finely powdered sodium iodide, and 100 c.c. of absolute alcohol was shaken for three hours in the cold, filtered, and the filtrate evaporated to dryness under diminished pressure. The residue was extracted with chloroform, and the filtered extract evaporated under diminished pressure until quite free from chloroform. A brownish-red oil, in amount corresponding with an almost theoretical conversion of dichloro- into di-iodo-arsine, was obtained, and was purified by crystallisation from alcohol, using solid carbon dioxide as an external refrigerant. In this way, pure phenyldi-iodoarsine was obtained in lemon-yellow clusters of needles melting (after remaining in contact with porous porcelain at a low temperature) at 15° (Found: I = 62·9.* M.W. [by cryoscopic method in benzene] = 393, 401. $C_6H_5I_2As$ requires I = 62·6 per cent. M.W. = 406).

Phenyldi-iodoarsine resembles the corresponding methyl and ethyl derivatives in odour and physiological properties. It undergoes slight decomposition when distilled under diminished pressure, boiling at 190°/12 mm. The effect of heat on the product obtained by Michaelis and Schulte (*Ber.*, 1881, **14**, 913), by the action of hydriodic acid on phenylarsenious oxide, shows that this product was, even before heating, a mixture of several substances.

Dimethyliodoarsine.

The difficulty of obtaining derivatives of cacodyl has now been removed by the discovery that Auger's method for the reduction of methylarsinic acid to methyldi-iodoarsine (*loc. cit.*) may be applied to the conversion of dimethylarsinic (cacodylic) acid into dimethyliodoarsine (cacodyl iodide).

A solution of 250 grams of cacodylic acid and 800 grams of potassium iodide in 1 litre of water was saturated with sulphur dioxide, dilute hydrochloric acid (500 c.c. of concentrated acid and

* All these compounds in which iodine and arsenic are directly combined (whether the arsenic be ter- or quinque-valent) react quantitatively with silver nitrate in alcoholic solution.

500 c.c. of water) being added from time to time. Reduction proceeded rapidly, with the separation of dimethyliodoarsine as a yellow oil, the end of the process being indicated by the separation also of sulphur. The oily layer was separated, dried over calcium chloride, and distilled, when pure dimethyliodoarsine (380 grams, corresponding with a 90 per cent. conversion) was obtained as a yellow liquid boiling at 154—157°, and freezing to a pale yellow, crystalline solid at about −35°.

From dimethyliodoarsine, cacodyl oxide, chloride, etc., may readily be prepared, without the production of intermediate compounds, which are spontaneously inflammable.

Phenylmethyliodoarsine and Phenylmethylchloroarsine.

By a similar reduction process, phenylmethylarsinic acid (Bertheim, *Ber.*, 1915, **48**, 350) has been converted into phenylmethyliodoarsine.

The phenylarsenious oxide required was prepared by treating phenyldichloroarsine with excess of powdered sodium hydrogen sulphite in the presence of a little water. On removing the inorganic matter by repeated extraction with hot water, the pure oxide was left behind, and, when cold, could be ground up, and was then used without further purification for conversion into phenylmethyliodoarsine.

Phenylarsenious oxide (50 grams) was dissolved in a solution of 30 grams of sodium hydroxide in 240 c.c. of rectified spirit and 60 c.c. of water, the solution cooled, and treated with 30 c.c. of methyl iodide. A vigorous reaction set in, and was allowed to complete itself overnight. The mixture was acidified, freed from alcohol by distillation, treated with 50 grams of potassium iodide, and saturated with sulphur dioxide. The dark oil formed was separated, dried over calcium chloride, and distilled, when 54 grams of phenylmethyliodoarsine, a yellow oil boiling at 138—140°/12 mm., were obtained (Found: I = 43·7. C_7H_8IAs requires I = 43·2 per cent.).

It is interesting to note that in this preparation sodium hydroxide gives better results than potassium hydroxide.

The preparation of the corresponding chloro-arsine is readily effected by treating the iodo-compound with the calculated amount of sodium hydroxide, washing the oily oxide so obtained with water, and subsequently shaking repeatedly with small quantities of concentrated hydrochloric acid. The oil, after being dried over calcium chloride, distils at 113·5°/14 mm. (Found: Cl = 17·6. C_7H_8ClAs requires Cl = 17·5 per cent.).

Phenylmethylchloroarsine is a pale yellow liquid resembling phenyldichloroarsine in appearance and physiological properties.

The so-called Bart reaction (D.R.-P. 250264) for the preparation of arsinic acids is unsatisfactory in the case of phenylmethylarsinic acid, and therefore of its reduction products, although a small quantity of phenylmethyliodoarsine was prepared in this manner, benzenediazonium chloride being combined with methylarsenious oxide in alkaline solution.

The ethylation of phenylarsenious oxide proceeds very much more slowly than the methylation, and is only partial under conditions that allow of quantitative methylation.

Phenyldimethylarsine.

This arsine was obtained in 75 per cent. yield by Winmill (T., 1912, **101**, 722) by the action of magnesium methyl iodide on phenyldichloroarsine in the presence of light petroleum. The following method gave even more satisfactory results.

A Grignard reagent, made by the interaction of 19 grams of bromobenzene, 2·9 grams of magnesium, and 50 c.c. of ether, was gradually treated with a solution of 23·2 grams of dimethyliodoarsine in 50 c.c. of ether. A vigorous reaction accompanied each addition of iodo-compound, and, after allowing the mixture to remain at the ordinary temperature for two hours, ice and dilute hydrochloric acid were added, the ethereal layer separated, and dried over anhydrous sodium sulphate. The ether was evaporated and the residue distilled under diminished pressure, when 16 grams of phenyldimethylarsine were obtained as a colourless oil boiling at 85°/14 mm., and possessing the properties ascribed to the arsine by Michaelis and Link (*Annalen*, 1881, **207**, 205). The methiodide melted at 250° (Michaelis and Link, *loc. cit.*, give 244°).

The *ethiodide* is obtained at water-bath temperatures, and crystallises from alcohol in colourless needles melting at 142°; mixtures with the methiodide of phenylmethylethylarsine melted at the same temperature, indicating the identity of the two substances.

The *benziodide* is readily formed, and crystallises from a mixture of acetone and ether in colourless needles melting at 115—116° (Found: I=31·5. $C_{15}H_{18}IAs$ requires I=31·8 per cent.).

Phenyldimethylarsine combines energetically with equimolecular quantities of certain halogenated arsines.

Compound, $PhMe_2As,MeAsI_2$.—This compound is formed from the arsine and methyldi-iodoarsine when the two substances are

mixed in equimolecular quantities. Heat is generated, and, after a few moments, the whole becomes solid. The product crystallises from a mixture of acetone and ether in lemon-yellow needles melting at 93—94° (Found: I = 48·3. M.W. [by cryoscopic method in benzene] = 259, 264. $C_9H_{14}I_2As_2$ requires I = 48·3 per cent. M.W. = 526).

The compound is therefore completely dissociated into phenyldimethylarsine and methyldi-iodoarsine in benzene solution at concentrations up to 5 per cent.

Action of Methyl Iodide on the Compound, $PhMe_2As,MeAsI_2$.

A solution of a small quantity of the compound in benzene, mixed with an excess of methyl iodide, deposited, after some hours, slender, colourless needles, which melted at 243° without purification, a mixture with pure phenyltrimethylarsonium iodide melting at 248°. The additive compound is quantitatively converted by methyl iodide into the methiodide of the arsine originally used.

Compound, $PhMe_2As,EtAsI_2$.—Phenyldimethylarsine combines readily with ethyldi-iodoarsine to give a yellow solid, which, when crystallised from alcohol, melts at 44° (Found: I = 47·2. M.W. [by cryoscopic method in benzene] = 264, 266. $C_{10}H_{16}I_2As_2$ requires I = 47·0 per cent. M.W. = 540).

Compound, $PhMe_2As,PhAsI_2$.—This compound, prepared by mixing the arsine and iodo-arsine in calculated quantities, crystallises from alcohol or acetone in orange-coloured prisms melting at 69° (Found: I = 43·3. M.W. [by cryoscopic method in benzene] = 286, 287. $C_{14}H_{16}I_2As_2$ requires I = 43·2 per cent. M.W. = 588).

This compound is of a deeper shade than those of the corresponding compounds from alkyldi-iodoarsines.

Compound, $PhMe_2As,PhAsCl_2$.—Phenyldimethylarsine combines readily with phenyldichloroarsine to give a colourless solid crystallising from alcohol in colourless needles melting at 36° (Found: Cl = 17·7. M.W. [by cryoscopic method in benzene] = 215, 212. $C_{14}H_{16}Cl_2As_2$ requires Cl = 17·5 per cent. M.W. = 405).

Phenyldiethylarsine.

Michaelis and La Coste (*Annalen*, 1880, **201**, 212) first obtained this arsine from zinc diethyl and phenyldichloroarsine in ethereal solution, Winmill (*loc. cit.*) subsequently showing that the reaction proceeded more satisfactorily in the presence of light petroleum. We have now by the following method eliminated the difficulty attached to these methods of preparation.

A Grignard reagent, prepared from 26·2 grams of ethyl bromide,

5·8 grams of magnesium, and 40 c.c. of ether, was gradually treated with a solution of 22·3 grams of phenyldichloroarsine in 100 c.c. of benzene, the mixture finally heated to boiling for two hours, and the ether allowed to distil off slowly. The resulting mixture was decomposed with ice and dilute sulphuric acid, the benzene layer separated, dried, and evaporated, and the residue distilled under diminished pressure, when 12 grams of phenyldiethylarsine were obtained as a colourless oil boiling at 111—115°/14 mm., a further 3 grams of slightly less pure arsine distilling at 115—120°/14 mm. The arsine possessed the properties ascribed to it in the literature.

The methiodide was described by Michaelis (*Annalen*, 1902, **320**, 296) as melting at 122°. We have been unable to confirm his statements, our results being as follows.

When phenyldiethylarsine and methyl iodide are mixed, heat is evolved and a dark oil separates, which only becomes crystalline after a considerable time or after scratching vigorously. This substance, after thorough purification by repeated crystallisation from alcohol, in the presence or absence of ether, was obtained as a colourless, crystalline solid melting at 75—77° (Found: I = 36·1. $C_{11}H_{18}IAs$ requires I = 36·1 per cent.).

The ethiodide and the methylene iodide additive compound were found to possess the properties ascribed to them by Michaelis (*loc. cit.*).

Compound, $PhEt_2As,MeAsI_2$.—This was formed readily, and crystallised from alcohol or acetone in bright yellow needles melting at 78—79° (Found: I = 45·4. M.W. [by cryoscopic method in benzene] = 271, 273. $C_{11}H_{18}I_2As_2$ requires I = 45·8. M.W. = 544).

Phenylmethylethylarsine.

Phenylmethyliodoarsine or the corresponding chloro-compound reacts vigorously with magnesium ethyl bromide to give the desired mixed arsine.

Phenylmethyliodoarsine (19 grams) dissolved in 50 c.c. of benzene was gradually added to a Grignard reagent, prepared from 7·8 grams of ethyl bromide, 1·7 grams of magnesium, and 20 c.c. of ether. When the whole of the iodo-compound had been added, the mixture was heated to boiling for two hours, decomposed, and worked up in the usual manner, when 8 grams of phenylmethylethylarsine were obtained as a colourless oil boiling at 97°/12—13 mm. (Found [by Ewins' method]: As = 37·8. $C_9H_{13}As$ requires As = 38·3 per cent.).

The arsine, as might be expected, possesses physical and chemical

properties intermediate between those of the dimethyl- and diethyl-arsine.

The *methiodide* is readily formed, and crystallises from alcohol in colourless needles melting at 142° (Found: I = 37·5. $C_{10}H_{16}IAs$ requires I = 37·6 per cent.).

Compound, PhMeEtAs,$MeAsI_2$.—This compound crystallises from alcohol in yellow needles melting at 84° (Found: I = 46·8. $C_{10}H_{16}I_2As_2$ requires I = 47·0 per cent.).

Compound, PhMeEtAs,$PhAsI_2$.—This substance separates from alcohol in orange-yellow prisms melting at 55° (Found: I = 42·3. M.W. [by cryoscopic method in benzene] = 315, 322, 327. $C_{15}H_{18}I_2As_2$ requires I = 42·2 per cent. M.W. = 602).

Diphenylmethylarsine.

The preparation of this arsine by the action of zinc dimethyl on diphenylchloroarsine (Michaelis and Link, *loc. cit.*) is less satisfactory than the following.

A Grignard reagent, prepared from 34·6 grams of bromobenzene, 5·4 grams of magnesium, and 80 c.c. of ether, was gradually treated with 34 grams of methyldi-iodoarsine after removal of unchanged magnesium by decantation. The product was worked up in the usual manner, and gave 17·5 grams of diphenylmethylarsine boiling at 163—170°/15 mm., and possessing the properties described in the literature.

This arsine possesses only to a slight degree the property of forming additive compounds, and, so far, no compounds have been obtained with alkyl- or phenyl-di-iodoarsines.

The *benziodide* melts at 193° (Found: I = 27·5. $C_{20}H_{20}IAs$ requires I = 27·5 per cent.).

α-Naphthyldimethylarsine.

Dimethyliodoarsine (46·4 grams) was gradually added to a Grignard reagent, prepared from 50 grams of α-bromonaphthalene, 5·34 grams of magnesium, and 200 c.c. of ether (if small quantities of ether are used, the magnesium α-naphthyl bromide separates out as a crystalline solid), the reaction allowed to become complete by heating to boiling for an hour, and the cooled product decomposed and worked up in the usual manner. In this way, 37 grams (instead of the theoretical quantity of 46 grams) of α-naphthyldimethylarsine were obtained boiling at 163—165°/13 mm.

The *methiodide* is formed very readily, and crystallises from alcohol in colourless needles melting at 230° (Found: I = 33·7. $C_{13}H_{16}IAs$ requires I = 34·0 per cent.).

The *ethiodide* is formed at 90—100°, and crystallises from alcohol in colourless leaflets melting at 218° (Found: I = 32·5. $C_{14}H_{18}IAs$ requires I = 32·7 per cent.).

Compound, $C_{10}H_7 \cdot Me_2As,MeAsI_2$.—This compound is readily formed, and crystallises from alcohol in yellow needles melting at 76—77° (Found: I = 44·0. $C_{13}H_{16}I_2As_2$ requires I = 44·1 per cent.).

Triphenylarsine.

Although triphenylarsine is readily prepared by the action of sodium on a mixture of chlorobenzene and arsenic chloride, the following method has been found to be the most convenient for the preparation of small quantities. More than 90 per cent. of the theoretical conversion can be effected, and the arsine requires very little purification.

Powdered arsenic iodide (22 grams) was gradually added, with shaking, to a Grignard reagent, prepared from 26 grams of bromobenzene, 4 grams of magnesium, and 50 c.c. of ether. The vigorous reaction having abated, the mixture was heated to the boiling point for half an hour, and then decomposed, etc., the more volatile products being removed by heating finally to 200° under 12 mm. pressure. The residue, practically pure triphenylarsine, when once crystallised from alcohol, melted correctly at 58°.

No additive compounds could be obtained between the arsine and any of the di-iodoarsines, a fact which falls in line with the difficulty of preparing the methiodide.

Tri-o-tolylarsine.

Arsenic iodide (22·8 grams) was added gradually to a Grignard reagent, prepared from 26 grams of *o*-bromotoluene, 3·7 grams of magnesium, and 80 c.c. of ether, the reaction completed by heating for a short time, and the product worked up as in the case of triphenylarsine. Ten grams of *tri-o-tolylarsine* were obtained, and were crystallised from alcohol, when colourless needles were formed melting at 98° (Found: As = 20·9. $C_{21}H_{21}As$ requires As = 21·5 per cent.).

The *methiodide* crystallises from water in colourless needles melting at 166°. Owing to the small quantity of material available for analysis, the determination of iodine was unsatisfactory (Found: I = 24·2. $C_{22}H_{24}IAs$ requires I = 25·9 per cent.).

Di-o-tolylmethylarsine.

A Grignard reagent was prepared from 22 grams of *o*-bromotoluene, 3·2 grams of magnesium, and 50 c.c. of ether. A solution of 18 grams of methyldi-iodoarsine in 100 c.c. of benzene was gradually added, the reaction completed by heating under reflux, and the product decomposed with ice and dilute sulphuric acid. The separated ether–benzene layer was washed with aqueous sodium hydroxide to remove unchanged methyldi-iodoarsine, dried over calcium chloride, evaporated, and the residue distilled under diminished pressure. In this way, 8 grams of a very pale yellow oil were obtained boiling at 178—182°/12 mm., and setting, on cooling, to a solid melting at 42° (Found: As=27·3. $C_{15}H_{17}As$ requires As=27·6 per cent.).

The *methiodide* is formed readily, and crystallises from water in colourless needles melting at 195° (Found: I=31·2. $C_{16}H_{20}IAs$ requires I=30·7 per cent.).

THE UNIVERSITY CHEMICAL LABORATORIES,
SYDNEY. [*Received, September 27th*, 1920.]

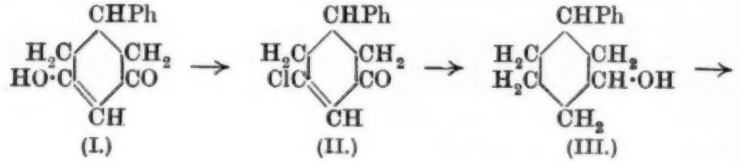
CL.—*Derivatives of Phenyldihydroresorcin.*

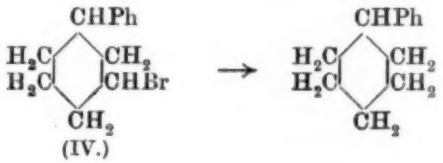
By ALEXANDER JOHN BOYD, PERCY HERBERT CLIFFORD, and MAURICE ERNEST PROBERT.

THE following is a brief account of some experiments commenced by one of us (A. J. B.) in 1914 at the suggestion of Professor A. W. Crossley: the work was interrupted, and could not be resumed until October, 1919, and although we (P. H. C. and M. E. P.) cannot now complete the original plan, it is thought advisable briefly to place on record such results as have been obtained.

The original object of the work was twofold; first, more fully to examine certain derivatives of phenyldihydroresorcin, because some of them, notably phenyl*cyclo*hexanol, had been encountered in the course of other experimental work then in progress (compare Crossley and Renouf, T., 1915, **107**, 608), and, secondly, to investigate the influence and behaviour of aromatic groups, such as phenyl, in hydroaromatic hydrocarbons. Phenyldihydroresorcin was therefore converted into phenyl*cyclo*hexane by a series of reactions which had been successfully employed in previous cases

(Crossley and Renouf, T., 1905, **87**, 1488). The dihydroresorcin (I), when treated with phosphorus trichloride, readily yields *chlorophenyl*cyclo*hexenone* (II), which, on reduction with sodium in moist ethereal solution, gives phenyl*cyclo*hexanol (III).





Hydrogen bromide converts the alcohol into *bromophenyl*cyclo*hexane* (IV), in which substance the bromine is readily displaced by hydrogen under the influence of zinc dust in aqueous-alcoholic solution, giving rise to phenyl*cyclo*hexane. The hydrocarbon is easily obtained in about 74 per cent. of the theoretical amount, and has all the properties previously ascribed to it by other workers.

Certain other derivatives of phenyldihydroresorcin were of necessity isolated in the course of the work, and they are described in the experimental part of this communication.

Experimental.

Phenyldihydroresorcin was prepared from ethyl malonate and styryl methyl ketone (benzylideneacetone), using the conditions described by Crossley and Renouf (T., 1915, **107**, 608). The latter was obtained from benzaldehyde and acetone, as described by Claisen and Ponder (*Annalen*, 1884, **223**, 139), but it was found that two vacuum distillations did not remove entirely the unchanged benzaldehyde, and the following procedure was therefore adopted to purify the ketone. The crude product was distilled once in a vacuum, and the distillate, which crystallised on cooling, was broken up, spread on a porous plate, and exposed to the air for two days. This caused oxidation of the benzaldehyde to benzoic acid, which was removed by washing with dilute sodium hydroxide solution. After further washing with water, the ketone was dried and crystallised from light petroleum (b. p. 60—80°).

Action of Bromine on Phenyldihydroresorcin.—Five grams of phenyldihydroresorcin (1 mol.) were suspended in 50 c.c. of dry chloroform, and a solution of 4·3 grams (2 atoms) of bromine in dry chloroform was gradually added with constant shaking, when the resorcin gradually dissolved. On further addition of bromine, much hydrogen bromide was evolved, and a bulky, white solid separated, which was collected, washed with chloroform, dried on a porous plate, and crystallised from aqueous alcohol (Found: Br = 29·95. $C_{12}H_{11}O_2Br$ requires Br = 29·96 per cent.).

4-*Bromophenyldihydroresorcin*, $CHPh\langle^{CH_2\cdot CO}_{CH_2\cdot CO}\rangle CHBr$, crystallises from aqueous alcohol in compact clusters of short, glistening needles melting at 177° with rapid evolution of gas. (If heated sufficiently rapidly, the melting point may be found as high as 189°.) It is soluble in alcohol, acetone, or ethyl acetate, sparingly so in chloroform or benzene on boiling, but insoluble in ether or light petroleum.

Oxidation of Phenyldihydroresorcin.—Five grams of the resorcin were suspended in 125 c.c. of water and treated with a 4 per cent. solution of potassium permanganate until the latter was no longer decolorised, the whole being continuously mechanically shaken. About five hours were required for the completion of the oxidation. The product, worked up in the usual way, gave 3·8 grams of a solid, from which were isolated, by repeated recrystallisation from dilute hydrochloric acid, two acids, *A* and *B*.

The acid *A* melted at 139°, nor was this melting point lowered on admixture with a specimen of pure β-phenylglutaric acid prepared for purposes of comparison (see p. 1387).

The acid *B* melted at 166·5—167°, and its melting point was not lowered when mixed with phenylsuccinic acid (see p. 1386 for the proof of the identity of this acid).

Owing to the great similarity in solubility of β-phenylglutaric acid and phenylsuccinic acid, it was not found possible to separate the whole of *A* and *B*, but there was no evidence of the presence of another compound in the remaining mixture.

Action of Phosphorus Trichloride on Phenyldihydroresorcin.—Sixty grams (3 mols.) of phenyldihydroresorcin were heated with 22 grams (1·5 mols.) of phosphorus trichloride and 240 grams of dry chloroform on a water-bath for three hours. After distilling off the chloroform, the residue was poured into cold water and extracted four times with ether, the ethereal solution thoroughly washed with sodium hydroxide solution (4 per cent.), then with water, dried over calcium chloride, and the ether evaporated. The oily residue, which readily solidified on cooling, was crystallised

twice from light petroleum (b. p. 60—80°) (Found: Cl = 17·00. $C_{12}H_{11}OCl$ requires Cl = 17·19 per cent.).

5-Chloro-1-phenyl-Δ^4*-cyclohexen-3-one*, $CHPh<\begin{matrix}CH_2\text{-}CO\\CH_2\cdot CCl\end{matrix}>CH$,

the yield of which is about 65 per cent. of the theoretical, crystallises in colourless, transparent plates melting at 63·5—64°. It possesses a rather pungent odour, is somewhat sternutatory, and has an irritating effect on the skin. It is soluble in alcohol, ether, chloroform, acetone, benzene, or ethyl acetate, and in light petroleum on boiling. When boiled with absolute alcohol, and the solution allowed to remain in a moist atmosphere for several days, the ketone reverts to phenyldihydroresorcin. There is evidence that the ethyl ether of phenyldihydroresorcin (Vorländer and Erig, *Annalen*, 1897, **294**, 304) is an intermediate product, but the change has not been fully investigated.

The *oxime* crystallises from alcohol in almost colourless, short needles, melting and decomposing at 157° (Found: N = 6·5. $C_{12}H_{12}ONCl$ requires N = 6·32 per cent.).

The *semicarbazone*, prepared in the usual manner, crystallises from alcohol in rosettes of small, colourless needles. When heated in a capillary tube, it softens at 150·5°, melts at 153·5°, and decomposes at 191°. It is insoluble in the usual organic solvents, with the exception of ether, benzene, and light petroleum, in which it is only very sparingly soluble, even on boiling (Found: N = 15·91. $C_{13}H_{14}ON_3Cl$ requires N = 15·94 per cent.).

Oxidation of Chlorophenylcyclohexenone.—Twenty grams of the chloro-ketone were suspended in 500 c.c. of water and treated with a 4 per cent. solution of potassium permanganate until the latter was no longer decolorised, the whole being continuously shaken mechanically. Oxidation took place slowly, requiring twenty hours for completion. The product, worked up in the usual way, gave 13·5 grams of solid, from which were isolated, by repeated recrystallisation from dilute hydrochloric acid solution, *A*, an acid melting at 167°; *B*, an acid melting at 138·5—139·5°; and *C*, a small quantity of an acid melting at 121—121·5°, which was obtained by extraction of the above mixture with cold benzene and recrystallisation of the residue obtained on evaporation of the solvent.

The acid (*A*) yielded an anhydride melting at 53—54° and an anilic acid melting at 169—170° when treated according to the directions given by Hann and Lapworth (T., 1904, **85**, 1366) for the preparation of these derivatives of phenylsuccinic acid. The fact that these data coincide with those given by Hann and Lapworth proves the acid (*A*) to be phenylsuccinic acid.

The melting point of the acid *B* was not lowered on admixture with pure β-phenylglutaric acid (m. p. 138—140°) prepared for the purposes of comparison (*Ber.*, 1899, **32**, 1879). On treating its silver salt with methyl iodide in dry ethereal solution, an ester resulted melting at 83·5—84·5°, nor was this melting point lowered on admixture with a specimen of the pure dimethyl ester of β-phenylglutaric acid (m. p. 84—85°) prepared for the purposes of comparison (*Ber.*, 1898, **31**, 1828).

Only a very small quantity of the acid *C* was obtained after recrystallisation from water. On admixture with pure benzoic acid, the melting point was not lowered appreciably, and, although the amount of the acid was too small to admit of further purification or preparation of derivatives, its odour and behaviour towards various solvents support the supposition that it is benzoic acid.

Reduction of Chlorophenylcyclohexenone.—Quantities of 20 grams of the chloro-ketone were treated with twice the calculated quantity of sodium in moist ethereal solution, as described by Crossley and Renouf (T., 1905, **87**, 1494). When all the sodium had dissolved, the ethereal solution was separated, washed with water until no longer alkaline, dried over anhydrous potassium carbonate, and the ether evaporated. The residue was submitted to steam distillation until a test portion of the distillate gave no turbidity on adding potassium carbonate. The distillate contained a solid in suspension, crystallising in colourless needles, which were collected and crystallised from light petroleum (b. p. 80—100°) (Found: C = 81·60; H = 9·36. $C_{12}H_{16}O$ requires C = 81·76; H = 9·16 per cent.).

1-Phenyl*cyclo*hexan-3-ol, $CHPh\begin{matrix}<CH_2\cdot CH(OH)\\CH_2\text{——}CH_2\end{matrix}>CH_2$, was prepared, although not fully described, by Crossley and Renouf (T., 1915, **107**, 608) for comparison with a by-product obtained in the reduction of phenyldihydroresorcin. It is obtained in 50—53 per cent. of the theoretical amount, and crystallises in fine, colourless needles melting at 79·5—80·5°, and possessing a pleasant odour somewhat resembling that of geranium. It is soluble in the usual organic solvents, but only sparingly so in cold light petroleum. When dissolved in absolute alcohol and the solution gradually treated with concentrated sulphuric acid, it gives a greenish-yellow colour, slowly changing to brown with a green fluorescence.

The *acetyl* derivative, prepared in the usual manner, crystallises from a small quantity of alcohol in stout, transparent, oblong plates melting at 43—44°, and is readily soluble in all the usual organic solvents. It can be distilled in air without decomposition

and boils at 300° (Found: C = 77·05; H = 8·69. $C_{14}H_{18}O_2$ requires C = 77·01; H = 8·32 per cent.).

The *benzoyl* derivative is readily obtained in quantitative yield. It crystallises from ethyl or methyl alcohol in rosettes of colourless prisms melting at 68°, and is readily soluble in all the usual organic solvents on boiling (Found: C = 81·28; H = 7·36. $C_{19}H_{20}O_2$ requires C = 81·39; H = 7·19 per cent.).

The o-*nitrobenzoyl* derivative was prepared by allowing molecular proportions of *o*-nitrobenzoyl chloride and the alcohol to react in pyridine solution. It crystallises from dilute solution in ethyl or methyl alcohol in rosettes of minute needles melting at 70° (Found: N = 4·49. $C_{19}H_{19}O_4N$ requires N = 4·31 per cent.).

*Action of Hydrogen Bromide on Phenyl*cyclo*hexan*-3-*ol*.—Quantities of 5 grams of the alcohol were sealed up in small soda-water bottles with 25 c.c. of fuming hydrobromic acid, saturated at 0°, and heated in a water-bath for one hour. The resulting liquid, which was in two layers, was poured into excess of cold water, and the lower, oily portion dissolved in ether. The ethereal solution was washed with water, then with dilute sodium carbonate solution, finally again with water, dried, and the ether removed, the residue being distilled under diminished pressure (Found: Br = 33·49. $C_{12}H_{15}Br$ requires Br = 33·42 per cent.).

3-*Bromo*-1-*phenyl*cyclo*hexane*, the yield of which is almost quantitative, is a clear, colourless liquid boiling at 186—187°/40 mm., with a pleasant odour resembling that of geraniol, yet somewhat reminiscent of the odour of oranges.

Action of Zinc Dust on 3-*Bromo*-1-*phenyl*cyclo*hexane*.—Twenty-four grams of bromophenyl*cyclo*hexane were mixed with 75 c.c. of 90 per cent. alcohol and sufficient absolute alcohol to form a clear solution, to which were added 38·5 grams of zinc dust mixed with an equal volume of sand, and the whole was heated on the water-bath for ten hours. The resulting liquid was poured into a large excess of water, the mixture extracted with ether, the ethereal solution washed with water, dried, and the ether evaporated, using a fractionating column. The resulting oil, which was nearly colourless, was heated over metallic sodium for two hours and then distilled, when 13 grams passed over at 232—233°, and, after one further distillation from sodium, 11·9 grams (yield, 74 per cent. of the theoretical) were obtained boiling constantly at 233—234°/755 mm. It readily solidified when cooled to just below 0°, and melted at 6·5°. These properties agree closely with previous descriptions of the properties of phenyl*cyclo*hexane (Willstätter and Lessing, *Ber.*, 1901, **34**, 506; Eijkman,

Chem. Weekblad, 1903, **1**, 7; Meerwein and Kremers, *Annalen*, 1919, **419**, 121).

In order further to establish its identity with phenyl*cyclo*hexane, 6 grams of the substance were treated with fuming nitric acid (D 1·50) until the addition of acid caused no further visible change (about 10 c.c. of acid were used). The mixture was poured into water, and the heavy, oily layer dissolved in ether and worked up in the usual manner. On evaporation of the ether, 7·9 grams of a yellow oil were obtained, which, on cooling, gave a crystalline deposit weighing 3·8 grams after drying on a porous plate. It crystallised from aqueous alcohol in large, colourless, lustrous leaflets melting at 57·5—58° (Kursanov, *Annalen*, 1901, **318**, 309, gives the melting point of *p*-nitrophenyl*cyclo*hexane as 57·5—58·5°).

*Preparation of Phenyl*cyclo*hexan-3-one*, $CHPh<^{CH_2-CO}_{CH_2\cdot CH_2}>CH_2$. —Fourteen grams of phenyl*cyclo*hexan-3-ol were added to 126 grams of Beckmann's chromic acid mixture [60 grams (1 mol.) of potassium dichromate and 50 grams (2·5 mols.) of sulphuric acid in 300 c.c. of water], the whole being well shaken. The temperature rose to 45°, when a reaction set in, which was soon complete. The mixture was then kept at 50—55° for thirty minutes, with constant shaking, extracted with ether, the ethereal solution worked up in the usual way, and dried. After evaporating the ether, the residual, colourless oil was distilled under diminished pressure, when 12·7 grams passed over at 169—169·5°/18 mm. (Found: C=82·52; H=8·42. $C_{12}H_{14}O$ requires C=82·72; H=8·10 per cent.).

1-*Phenyl*cyclo*hexan*-3-*one*, the yield of which is practically quantitative, is a colourless liquid boiling at 169—169·5°/18 mm. and 287—288°/736 mm., which does not solidify when cooled to −10°. With alcoholic sulphuric acid it gives a reddish-yellow solution with a green fluorescence.

The *semicarbazone*, prepared in the usual manner, crystallises from alcohol in radiating clusters of glistening prisms melting at 167°. It is soluble in methyl or ethyl alcohol, chloroform, or ethyl acetate, and in acetone, benzene, or light petroleum on boiling, but only very sparingly so in ether (Found: N=18·22. $C_{13}H_{17}ON_3$ requires N=18·18 per cent.).

The *oxime* crystallises from alcohol in colourless, ill-defined plates, which melt at 128—129°, but begin to shrink at about 120°. It is insoluble in light petroleum and only sparingly soluble in ether, but dissolves readily in the other usual organic

solvents, especially on warming (Found: N = 7·34. $C_{12}H_{15}ON$ requires N = 7·41 per cent.).

The authors desire to express their sincere thanks to Professor Crossley for originally suggesting the work and for the help given by him during its progress.

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CLI.—*The Electrical Conductivity of Potassium, Sodium, and Barium Chlorides in Mixtures of Pyridine and Water.*

By JNANENDRA CHANDRA GHOSH.

IN previous papers (T., 1918, **113**, 449, 627) it has been shown that in solutions of strong electrolytes, the increase in molecular conductivity with dilution is given by the following equations:

$$\frac{N.E^2\sqrt[3]{2N}}{D\sqrt[3]{V}} = 2RT\log_e\frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for univalent binary electrolytes, and

$$\frac{6N.E^2\sqrt[3]{2N}}{D\sqrt{3}\sqrt[3]{V}} = 3RT\log_e\frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad (2)$$

for uni-bivalent electrolytes, where N is Avogadro's number, E the absolute charge on an ion, V the molecular dilution, and D the dielectric constant of the solvent. Equations (1) and (2) contain the term μ_∞, the molecular conductivity at infinite dilution, which cannot be determined experimentally. They can, however, be easily put in the following forms, which contain no unknown magnitudes whatsoever:

$$\frac{N.E^2\sqrt[3]{2N}}{D.2RT}\left(\frac{1}{\sqrt[3]{V_1}} - \frac{1}{\sqrt[3]{V_2}}\right) = \log_e\frac{\mu_{v_2}}{\mu_{v_1}} \quad . \quad . \quad . \quad (3)$$

and

$$\frac{6N.E^2.\sqrt[3]{2N}}{D.\sqrt{3}.3RT}\left(\frac{1}{\sqrt[3]{V_1}} - \frac{1}{\sqrt[3]{V_2}}\right) = \log_e\frac{\mu_{v_2}}{\mu_{v_1}} \quad . \quad . \quad . \quad (4)$$

The present investigation was carried out with the object of testing the validity of the above relation between the dielectric constant of the solvent and variation of molecular conductivity with dilution.

It has already been shown that the extensive experimental data of Walden on the molecular conductivity of tetraethylammonium iodide in various solvents can be accounted for (with the exception of the aldehydes) on the assumption that tetraethylammonium iodide at first undergoes polymerisation, and then the double molecule dissociates as a uni-bivalent electrolyte. The experimental difficulties in determining molecular conductivity in pure non-aqueous solvents are very great. The data of different observers do not very often agree at all, and it was therefore concluded that the agreement between the observed and calculated value of molecular conductivity was within the limits of experimental error. In the present investigation, only the chlorides of potassium, sodium, and barium were used, which, unlike the iodide, have very little tendency to complex-formation. Binary mixtures of pyridine and water were selected, as they are completely miscible in one another, and offer a very wide range of dielectric constants varying from 12 to 80.

Preparation of Materials.

Chemically pure pyridine was distilled several times over solid potassium hydroxide, and the fraction distilling at 115—116° was collected. This fraction was then allowed to remain overnight over pieces of metallic sodium, as recommended by Hopkins (this vol., p. 280). Gas bubbles were evolved, showing that moisture was present. The dry substance was distilled directly into a dry flask protected from moisture by a calcium chloride tube. The specific conductivity at 18° was $0{\cdot}2 \times 10^{-6}$ mho, and the boiling point 115·6°.

Water was purified by distillation from acid and alkaline permanganates, a block-tin condenser being used. It was finally distilled from a quartz distillation apparatus, and stored in quartz flasks. The specific conductivity of the water was $1{\cdot}2 \times 10^{-6}$ mho at 18°. The mixtures of pure pyridine and water were also stored in quartz flasks.

The salts were crystallised twice from pure samples and dried by heating in a platinum crucible.

For experiments at 0°, a bath containing finely powdered ice was used, jacketed by a second vessel containing ice. The temperature varied from 0° to 0·05°. For experiments at 18°, a thermostat was used, the extreme variation of temperature being 0·02°. For

dilutions below 1000 litres, a closed conductivity cell made of Jena resistance glass was used, and for higher dilutions, a closed quartz cell, made by the British Silica Syndicate.

The bridge wire was carefully calibrated, and the resistances were National Physical Laboratory standards of 1, 10, 100, and 1000 ohms.

Dielectric Constants of Mixtures of Pyridine and Water.

The Nernst method was employed as modified by Turner (*Zeitsch. physikal. Chem.*, 1900, **35**, 385). A Wehnelt interrupter was used in the primary circuit of the secondary coil; it consisted of two thin platinum wires dipped in dilute sulphuric acid. The anode could be raised up and down by means of a rack and pinion arrangement, and a sharp, fine tone obtained at 16 volts by careful adjustment. The dielectric constant of pure pyridine at 0°, with chemically pure benzene as the liquid for comparison, was found to be 12·5 from the equation

$$D = (D_0 - 1)\frac{S - s}{s_0 - s} + 1,$$

where D_0 is the dielectric constant of the known substance, s the number of scale divisions the condenser plate has to be moved when the vessel is empty, s_0 the number for the substance of known dielectric constant, and S for the unknown substance. For binary mixtures of water and pyridine, pure pyridine was used as the comparison liquid, and the dielectric vessel consisted of a platinum crucible, and a platinum disk attached to the end of a platinum rod passing through a hole in the ebonite cover of the crucible.

Although pure pyridine and pure water have themselves very little specific conductivity, the conductivity of the binary mixture increases with increasing proportion of water, and for a mixture containing 90 per cent. of water, it is as high as 10×10^{-6} mho at 18°. The data for the dielectric constants of the mixtures containing a large proportion of water are therefore not very accurate, as it is very difficult to get a sharp sound minimum in the telephone.

TABLE I.

Percentage by weight of pyridine in water.	Dielectric constant at 0°.	Dielectric constant at 18°.
96·0	13·0	12·5
92·5	15·3	16·0
80·0	22·9	21·0
67·0	27·7	25·1
60·0	40·0	37·0
40·0	56·4	52·2
20·0	68·3	64·1

Molecular Conductivity of Salts in Mixtures of Pyridine and Water.

Mixtures containing 80 or 60 per cent. by weight of pyridine do not dissolve the chlorides of barium, potassium, and sodium easily. A definite amount of salt was therefore first dissolved in a given quantity of pure water, and pyridine then added. Barium chloride is not very readily soluble in these mixed solvents. Even in the case of $N/40$-solutions, crystals generally separate on keeping overnight. The state of supersaturation can, however, be easily maintained for the few hours necessary for taking a complete set of readings at various dilutions.

The molecular conductivity of the solutions is rather small, and hence the correction for the conductivity of the solvent becomes quite appreciable when the dilution is 80. The accuracy of the data for higher dilution depends on this solvent correction, and it was therefore necessary to determine the specific conductivity of the solvents every few hours. In tables II, III, IV, V, VI, and VII are given the observed values of equivalent conductivities at 0° and 18°. They are compared with those calculated from the observed value of λ_{160} from equation (3) in the case of uni-

TABLE II.

$t = 0°$.

Solvent containing 40 per cent. by weight of pyridine.

Salt.	$V =$	10.	40.	80.	640.	2560.
NaCl	λ obs.	22·1	24·6	25·5	27·6	28·6
	λ calc. from λ_{160} obs. = 26·3	22·5	24·8	25·6	27·4	28·1
KCl	λ obs.	25·6	28·3	29·3	31·4	32·2
	λ calc. from λ_{160} obs. = 30·0	25·9	28·2	29·2	31·1	31·8
$BaCl_2$	λ obs.	20·0	23·6	—	27·7	29·0
	λ calc. from λ_{160} obs. = 26·1	19·6	23·4	—	28·0	29·3

TABLE III.

$t = 0°$.

Solvent containing 60 per cent. by weight of pyridine.

Salt.	$V =$	10.	20.	40.	80.	640.	2560.
NaCl	λ obs.....	12·7	—	14·8	—	17·3	18·0
	λ calc. from λ_{160} obs. = 16·1	12·9	—	14·8	—	17·0	17·5
KCl	λ obs.....	—	14·55	15·7	16·5	18·3	19·1
	λ calc. from λ_{160} obs. = 17·2	—	14·80	15·7	16·5	18·2	18·8
$BaCl_2$	λ obs.....	10·2	—	12·9	—	16·1	17·0
	λ calc. from λ_{160} obs. = 14·8	9·9	—	12·7	—	16·3	17·3

TABLE IV.

$t = 0°$.

Solvent containing 80 per cent. by weight of pyridine.

Salt.		V =	20.	40.	80.	640.	5120.
NaCl	λ obs.		8·9	10·1	—	13·5	15·2
	λ calc. from λ_{160} obs. = 12·1	....	9·4	10·4	—	13·2	14·4
KCl	λ obs.		—	10·1	10·8	13·8	15·5
	λ calc. from λ_{160} obs. = 11·9	....	—	10·3	11·1	13·1	14·3

TABLE V.

$t = 18°$.

Solvent containing 40 per cent. by weight of pyridine.

Salt.		V =	10.	40.	80.	640.	2560
NaCl	λ obs.		40·4	44·6	46·5	50·1	51·8
	λ calc. from λ_{160} obs. = 47·9	....	40·9	45·1	46·7	49·8	51·1
KCl	λ obs.		46·8	51·5	53·8	57·8	59·4
	λ calc. from λ_{160} obs. = 55·6	....	47·4	52·3	54·1	57·8	59·2
$BaCl_2$	λ obs.		38·2	44·2	—	53·5	55·6
	λ calc. from λ_{160} obs. = 50·1	....	37·5	44·8	—	53·8	56·2

TABLE VI.

$t = 18°$.

Solvent containing 60 per cent. by weight of pyridine.

Salt.		V =	10.	20.	40.	80.	640.	2560.
NaCl	λ obs.		25·1	—	29·4	—	34·1	35·2
	λ calc. from λ_{160} obs. = 32·0		25·6	—	29·5	—	33·6	34·7
KCl	λ obs.		—	28·6	31·0	32·3	35·8	37·5
	λ calc. from λ_{160} obs. = 34·1		—	29·4	31·3	32·8	35·9	37·3
$BaCl_2$	λ obs.		19·6	—	24·9	—	31·4	33·2
	λ calc. from λ_{160} obs. = 28·7		19·1	—	24·5	—	31·7	33·8

TABLE VII.

$t = 18°$.

Solvent containing 80 per cent. by weight of pyridine.

Salt.		V =	20.	40.	80.	640.	5120
NaCl	λ obs.		17·2	19·5	—	26·3	29·9
	λ calc. from λ_{160} obs. = 23·4	....	18·1	20·1	—	25·8	27·9
KCl	λ obs.		—	19·1	21·0	25·0	28·9
	λ calc. from λ_{160} obs. = 22·7	....	—	19·5	21·2	25·2	27·3

univalent salts, and from equation (4) in the case of barium chloride. In the tables, V is the equivalent dilution in litres and λ the equivalent conductivity.

It will be noticed from the above tables that the agreement between the observed and calculated values of equivalent conductivities are within the limits of experimental error, except in the case of the solvent containing 80 per cent. by weight of pyridine. Here the extreme deviations between the observed and calculated values are as much as 7 per cent. Perhaps in the mixed solvent rich in pyridine there is a slight complex-formation. Hartley, Thomas, and Applebey (T., 1908, **93**, 538) have determined the molecular conductivity of lithium nitrate in mixtures of varying proportions of pyridine and water. It appears interesting to examine whether their experimental data agree with those calculated from equation (3). The observed values of molecular conductivity in table VIII are taken from their paper.

TABLE VIII.

$t = 25°$. Salt: Lithium Nitrate.

Mol. per cent. of pyridine in solvent.	V =	16.	32.	64.	128.	256.	512.	1024.
83·98	λ obs.	20·1	24·4	27·5	32·1	35·4	38·3	—
	λ calc from λ_8 obs. = 15·8	19·3	23·3	27·5	31·9	36·1	40·1	—
73·76	λ obs.	23·1	26·5	30·3	33·2	35·9	38·1	40·5
	λ calc. from λ_8 obs. = 19·1	22·9	26·8	30·3	33·8	37·0	39·6	41·6
46·67	λ obs.	24·9	27·4	29·5	30·7	32·2	33·2	—
	λ calc. from λ_8 obs. = 21·5	24·4	26·6	28·4	30·0	31·2	31·9	—
31·28	λ obs.	27·5	29·4	31·0	32·4	33·5	34·4	—
	λ calc. from λ_8 obs. = 25·2	27·4	29·1	30·4	31·4	32·2	32·5	—
5·71	λ obs.	60·8	63·1	64·9	66·3	67·5	68·5	69·5
	λ calc. from λ_8 obs. = 58·1	61·0	63·3	65·1	66·7	67·6	68·2	68·5

It will be at once seen that the agreement between the observed and calculated values of molecular conductivity is quite satisfactory. It is peculiar that in the solvent containing a 46·67 molecular percentage of pyridine, which is equivalent to 79 per cent. by weight of pyridine, the observed values of equivalent conductivity for lithium nitrate agree with the calculated values within the limits of experimental error. It is strange that the simpler salts, like potassium and sodium chlorides, should show greater deviations.

Viscosity of Mixtures of Pyridine and Water.

Hartley, Thomas, and Applebey (*loc. cit.*), and Dunstan and Thole (T., 1907, **91**, 1728), have determined the viscosity of mixtures of pyridine and water at 0° and 25°. No simple relation like that discovered by Walden between the molecular conductivity and viscosity of the solvent in solutions of tetraethylammonium iodide exists here. Following the lead of Bousfield, Hartley, Thomas, and Applebey conclude from the comparison of viscosity and conductivity data of lithium nitrate in mixtures of pyridine and water that there is a change in the size of the solvent atmosphere attached to the ions as the composition of the solvent changes. Although speculations in this field do not lead to tangible results, it was thought advisable to complete the investigation by determining the viscosities of the mixed solvents used in this investigation at 18°. For this purpose, a Dunstan and Thole type of viscosimeter was used. The results are given in table IX.

TABLE IX.

Percentage of pyridine in the solvent mixture.	Viscosity of the solvent mixture relative to water at 18°.
80	2·375
60	2·572
40	2·153

It will be observed that the conductivity of the salts continually increases as the percentage of pyridine in the solvent diminishes from 80 to 40. The viscosity of the mixture of pyridine and water, however, passes through a maximum, when the percentage by weight of pyridine is approximately 65.

Conclusion.

The molecular conductivity of the chlorides of potassium, sodium, and barium in mixtures of pyridine and water was studied. The dielectric constants of the solvents varied from 12 to 68; the experimental data confirm the hypothesis of complete ionisation of strong electrolytes as developed by the author.

My best thanks are due to Prof. F. G. Donnan, F.R.S., for his kind interest and help in providing the apparatus necessary for this investigation, and to my friend Mr. J. N. Mukherjee.

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CLII.—*The System Benzene–Ethyl Alcohol–Water between +25° and −5°.*

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Several investigations have been made on parts of this system at various temperatures, but no complete study has yet been published of the conditions of separation of solid benzene from a mixture of the three components.

This question is of general theoretical interest, and also of some practical importance, in view of the use of mixtures of benzene and alcohol as motor fuel.

Considering, first, the two-component systems involved, the system water–benzene is soon disposed of. The mutual solubilities at any temperatures with which we are concerned are very small. At 23°, the solubility of water in benzene is 0·061 per cent.* (Groschuff, *Zeitsch. Elektrochem.*, 1911, **17**, 348); at 15°, that of benzene in water is 0·15 per cent. (Moore and Roaf, *Proc. Roy. Soc.*, 1905, [*B*], **77**, 96). If we assume that the solubilities change with temperature in the same proportion as the vapour pressures, their values near the triple point (5·4°) will be: water in benzene 0·082, benzene in water 0·092 per cent. The temperature of the triple point, solid benzene–liquid benzene–water, has been found to be 5·39° (Sidgwick, this vol., p. 1340)—one-tenth of a degree below the freezing point of benzene; that of the triple point, ice–water–benzene, is by calculation −0·016°, the solubility of the benzene at this temperature being 0·069 per cent.

The system water–alcohol also scarcely concerns us. The freezing-point curve of solutions of water in alcohol has been measured (for example, by Pickering, T., 1893, **63**, 1015); a 10 per cent. solution freezes at about −4·6°, but the solubility of benzene in such a solution is so small that we did not investigate the ice curve.

The system benzene–ethyl alcohol is of much greater importance. The freezing-point curve has been examined by several observers. Our own results (extrapolated for anhydrous alcohol) are nearest to those of Pickering (*loc. cit.*, p. 1019), with whom Viala (*Bull. Soc. chim.*, 1914, [iv], **15**, 5) and Rózsa (*Zeitsch. Elektrochem.*, 1911, **17**, 934) also agree fairly closely. McIntosh (*J. Physical Chem.*, 1896, **1**, 480), who also measured this curve, states that his

* All solubilities in this paper are expressed in grams of solute per 100 grams of solution.

alcohol may have contained water; from our results, it seems that it must have contained about 4 per cent.

The three-component system has been examined by McIntosh (*loc. cit.*), Taylor (*J. Physical Chem.*, 1896, **1**, 301, 461), Lincoln (*ibid.*, 1900, **4**, 176), Bonner (*ibid.*, 1910, **14**, 779), and Rózsa (*loc. cit.*). McIntosh investigated the freezing point of the benzene, and drew attention to the remarkable fact that the freezing point of benzene containing alcohol is raised by the addition of water; he correctly explained this as being due to the increase of the vapour pressure of benzene on addition of a component in which it is insoluble, but his numerical results are vitiated by the presence of water in his original alcohol. Taylor, Lincoln, and Bonner examined the two-liquid equilibrium between 10° and 25°, and determined the composition of the conjugate solutions (tie-lines). Rózsa investigated the system both above and below the freezing point; his results are difficult to understand, as he does not define his concentrations, but on the most probable hypothesis they are roughly in agreement with ours.

These results taken together give an incomplete account of the behaviour of the system in the neighbourhood of the freezing point of benzene. We have endeavoured to extend and complete them.

Experimental.

The method adopted was to prepare mixtures of alcohol and water of known strength; these were mixed with various known proportions of benzene, and the temperature was determined at which the liquid separated into two layers or the benzene crystallised out. The concentrations are always expressed in grams of component per 100 grams of solution.

The alcohol was obtained by distilling ordinary "absolute" alcohol with lime; the percentage of water in it was determined from the density, using the tables given in the last edition of Beilstein's "Handbuch der Organischen Chemie." From this, the requisite aqueous mixtures were prepared gravimetrically. The purest alcohol used (99·5 per cent.) was obtained from this by redistillation after treatment with anhydrous copper sulphate.

The benzene was freed from thiophen by sulphuric acid, and frozen out seven times; it was then distilled over sodium.

The apparatus consisted of an ordinary Beckmann tube with air-jacket, thermometer, and stirrer. A known weight of one of the liquids was placed in it, and successive amounts (usually 1 c.c.) of the other added through the side-tube from an accurate pipette, which had been carefully graduated by weight with the particular

liquid to be used in it. The tube was warmed or cooled by a bath of water, ice, or ice and salt.

The thermometers had been compared with an instrument standardised at the Reichsanstalt, and were checked by redeterminations of the ice-point. The readings were corrected, when necessary, for the emergent stem. At high concentrations of benzene, the method of supercooling could be used, as the amount of solid benzene separating did not seriously affect the proportions. At lower concentrations, the point was observed at which the last

TABLE I.

Alcohol, 99·5 per cent.

Benzene. Per cent.	Temp.
92·42	+2·95°
80·29	1·26
75·32	0·50
70·92	−0·14
67·05	−0·86
62·05	−1·94
57·85	−2·94
54·16	−4·16
50·95	−5·42

Alcohol, 98·0 per cent.

95·20	+3·50
93·09	3·10
91·12	2·76
86·86	2·22
81·82	1·62
77·15	1·08
69·23	0·03
65·56	−0·72
58·76	−2·16
53·30	−3·90
50·55	−4·62
48·30	−5·72

Alcohol, 95·76 per cent.

94·50	+3·48
89·60	2·84
81·15	1·86
77·51	1·48
65·70	0·12
59·35	−1·04
55·46	−1·92
52·04	−2·75
49·02	−3·62
46·34	−4·42
43·94	−5·34

Alcohol, 90·06 per cent.

89·18	+30·7 (*L*)
87·55	26·1 (*L*)
86·88	23·9 (*L*)

Alcohol, 90·06 per cent. —*contd.*

Benzene. Per cent.	Temp.
85·24	16·1° (*L*)
84·30	11·0 (*L*)
83·18	5·2 (*L*)
82·54	2·0 (*L*)
81·19	2·51
74·22	2·13
68·33	1·78
59·42	0·95
55·60	0·42
49·31	− 0·51
46·62	− 0·91
42·09	− 1·97
37·65	− 3·54
35·76	− 4·30
34·05	− 5·14

Alcohol, 86·0 per cent.

73·89	+28·3 (*L*)
72·81	22·7 (*L*)
71·63	17·6 (*L*)
70·35	12·9 (*L*)
68·93	8·5 (*L*)
67·38	4·5 (*L*)

Alcohol, 80·10 per cent.

63·52	+39·2 (*L*)
61·66	32·1 (*L*)
57·41	19·6 (*L*)
50·55	9·2 (*L*)
47·14	5·2 (*L*)
44·19	1·6 (*L*)
44·19	2·45
39·24	2·00
33·03	0·96
30·64	0·30
26·78	− 1·12
25·18	− 2·02
23·76	− 2·97
22·50	− 3·75
21·36	− 4·67

Alcohol, 74·48 per cent.

Benzene. Per cent.	Temp.
44·43	+29·5° (*L*)
38·23	20·3 (*L*)
35·12	15·2 (*L*)
31·02	7·75 (*L*)
28·90	3·00 (*L*)
27·04	− 1·25 (*L*)
27·04	+ 2·30
24·03	+ 1·20
18·64	− 2·25
17·65	− 3·10
15·96	− 4·85

Alcohol, 69·08 per cent.

27·67	+25·3 (*L*)
25·88	21·2 (*L*)
24·31	17·3 (*L*)
22·91	13·5 (*L*)
21·67	9·9 (*L*)
20·55	6·5 (*L*)
19·06	1·95 (*L*)
18·20	2·30
17·15	1·52
15·37	0·02
13·72	− 1·34
12·37	− 3·02
11·81	− 3·70

Alcohol, 57·66 per cent.

10·53	+15·4 (*L*)
10·05	12·15 (*L*)
9·25	7·1 (*L*)
8·56	2·3 (*L*)
8·27	− 0·40 (*L*)
8·27	+ 2·15
6·66	− 2·92
6·34	− 4·20

Alcohol, 39 per cent

Less than 1·0	+25·0 (*L*)

crystals remained in equilibrium with the liquid. For the two-liquid equilibria, the point was taken at which the liquid, on slow cooling, became sufficiently turbid to obscure a bright object placed behind it.

The results are given in table I (p. 1399). The temperature is in every case the mean of two or three concordant observations; these, in the solutions containing more benzene, did not differ by more than 0·1°, but in the weaker solutions differences of as much as 0·25° could not always be avoided.

Each series in the table was carried out with alcohol of the strength stated at the head; the percentage of benzene given in the first column is the number of grams in 100 grams of the resulting mixture. The points marked (*L*) are those in which the separation was into two liquids; in all other cases they are the freezing points of the benzene. One or two solutions gave points of both kinds, a higher (stable) solid and a lower (metastable) liquid point.

From the curves, the values for a series of round temperatures were interpolated, and these are collected in table II. The first column gives the temperature, the second the freezing points of mixtures of benzene and anhydrous alcohol from the results of Pickering (*loc. cit.*); the other columns are from our own experiments. The two-liquid points are distinguished by an asterisk. The total composition of any liquid is, of course, obtained thus: the percentage of benzene is that given in the table; the percentage of water or alcohol is obtained by multiplying the difference between this and 100 by the proportion of water or alcohol (from the figure at the top of the column) in the aqueous alcohol used. At the foot of each column is given the percentage of benzene and the temperature at the triple point solution I–solution II–solid benzene.

The results are plotted for temperatures from +5° to −5° in Fig. 1, the full lines representing two-liquid and the dotted lines liquid–solid equilibria.

Discussion of Results.

The equilibrium of a three-component system can be expressed only by a solid diagram; this can take the form of a triangular prism, the isothermal curves being represented on a series of triangles. Each of the curves obtained by adding varying quantities of benzene to aqueous alcohol of a definite strength (which are plotted in Fig. 1) represents a section of this solid diagram by a plane which contains the temperature axis passing through the

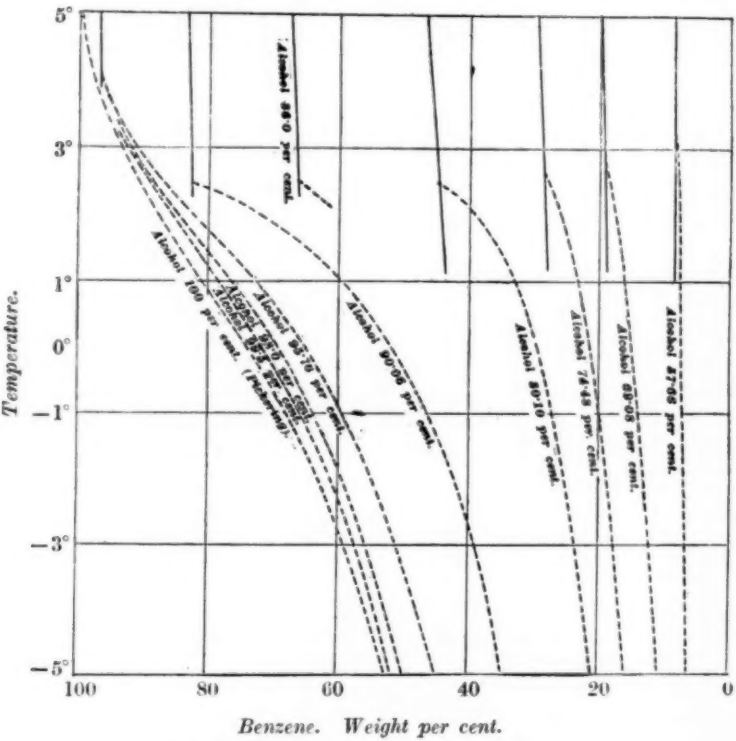
Table II.

The first line gives the percentage of alcohol in the mixture of alcohol and water employed, the other figures the percentage of benzene in the liquid at equilibrium.

Alcohol, per cent.:	100 Pickering	99·5	98·0	95·76	90·06	86·0	80·10	74·48	69·08	57·66	39·0
25°	—	—	—	—	87·22*	73·25*	59·41*	41·32*	27·46*	12·61*	1·0*
15	—	—	—	—	85·05*	70·95*	55·00*	35·10*	23·38*	10·47*	—
5	99·48	—	—	—	83·05*	67·65*	46·92*	29·81*	20·08*	8·95*	—
4	97·57	—	—	—	82·95*	—	46·18*	29·32*	19·75*	8·81*	—
3	93·82	92·65	92·52	91·22	82·76*	—	45·42*	28·85*	19·45*	8·68*	—
3	—	—	—	—	—	—	—	—	—	8·61	—
2	87·90	85·28	85·06	82·64	71·90	—	39·24	26·00	17·70	8·21	—
2	—	—	—	—	82·55*	—	44·50*	28·46*	19·10*	8·55*	—
1	80·89	78·36	76·58	72·78	59·80	—	33·15	23·60	16·45	7·86	—
1	—	—	—	—	82·35*	—	43·70*	27·95*	18·78*	8·44*	—
0	74·08	71·87	69·25	65·03	52·01	—	29·85	21·74	15·35	7·53	—
0	—	—	—	—	82·10*	—	43·08*	27·59*	18·48*	8·32*	—
− 1	67·79	66·45	63·93	59·48	46·39	—	27·34	20·11	14·25	7·22	—
− 2	62·87	61·70	59·62	55·07	42·00	—	25·40	18·93	13·27	6·93	—
− 3	59·10	57·54	56·00	51·17	39·00	—	23·52	17·80	12·40	6·65	—
− 4	55·56	54·49	52·71	47·82	37·48	—	22·21	16·75	11·56	6·38	—
− 5	52·60	51·85	49·90	44·81	34·45	—	21·00	15·82	10·80	6·12	—
Triple Point	—	—	—	96·76 +4·10°	82·62 +2·55°	66·38 +2·52°	44·95 +2·50°	28·75 +2·64°	19·28 +2·86°	8·70 +3·20°	—

benzene edge of the prism, and cuts the opposite side along a vertical line corresponding with the particular mixture of alcohol and water employed. The isothermals for three temperatures, namely, $+25°$, $+3°$, and $-5°$, are plotted on the triangle in Fig. 2. At 25° there is, of course, only the two-liquid equilibrium represented by the innermost curve. The dotted tie-lines, giving

FIG. 1.



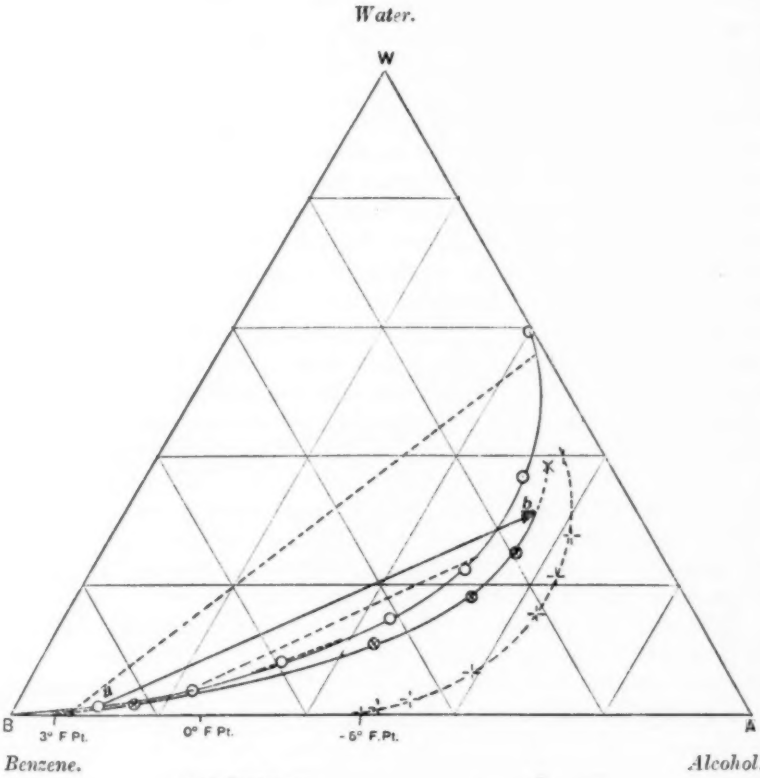
Full lines: Liquid–liquid equilibria.
Dotted lines: liquid–solid ,,

the compositions of the two liquids in equilibrium with one another, are taken from Taylor's measurements (*loc. cit.*).

At temperatures below 5·49°, solid benzene is present at B (pure benzene), and extends further along BA as the temperature falls. At $+3°$, for example, the solid is in equilibrium with a mixture of benzene and alcohol containing 6·18 per cent. of the latter. If water is added to this mixture, the freezing point of the benzene is raised, because the water, being insoluble in the benzene,

increases its vapour pressure. In order, therefore, to remain in the 3° isotherm, if water is added, alcohol must also be added; the solid–liquid curve (the dotted line) will thus incline to the right. Our results show that when it has reached the point *a*, a second

FIG. 2.



liquid phase appears; we have now reached the triple line, solid benzene–solution I–solution II (conveniently written S–L_1–L_2). This new liquid is the conjugate solution, the composition of which is given by the point *b*, which is at the other end of the tie-line *ab*; being in equilibrium with the first liquid, it must have the

same pressure of benzene vapour, and so must also freeze at 3°. Thus at 3° the L_1–L_2 part of the curve is confined to the part *ab*; at *b* the solid curve begins again, passing between the two-liquid curve and the side *AW*.

The triple line, that is, the curve joining the whole series of triple points S–L_1–L_2 for all mixtures of alcohol and water on addition of benzene, will begin on the line *BW* (no alcohol) at 5·39° (triple point, water–benzene liquid–benzene solid) at two points corresponding, respectively, with 99·97 and 0·092 per cent. of benzene. As successive quantities of alcohol are added, the temperature of the triple points will fall, but at any given temperature (not too low) there will be two triple points corresponding with two conjugate solutions joined by a tie-line; these points will move towards one another with a fall in temperature as the alcohol increases, but more rapidly from the water than from the benzene side (owing to the position of the tie-lines), until they finally meet at the plait-point, where the tie-lines vanish. The temperature of this point is the lowest at which two liquid phases made up of water, alcohol, and benzene can co-exist. Our results show that this temperature is +2·50°, and the composition of the liquid about 80 per cent. of benzene and 2 per cent. of water; at 25° Taylor found at the plait-point 80·2 per cent. of benzene.

At −5° no second liquid can exist. The solid benzene curve has the form of the outer dotted line; somewhere near the water end it must meet the ice-curve, which at −5° starts on *AW* at 91 per cent. of water, but the solubility of benzene in this region is so small that it could not be investigated.

One point of practical importance may be mentioned, in view of the use of these mixtures for motor fuel. If a fourth component (another hydrocarbon) were added, the freezing point of the benzene would be proportionately lowered (some 5° for 10 per cent.), but if a paraffin were used for this purpose, it would certainly increase the tendency of the liquid to separate into two layers. The solubility of paraffins in alcohol containing water is extraordinarily small. The system hexane–alcohol–water has been examined at 0° by Bonner (*loc. cit.*, p. 777); the heterogeneous area occupies nearly the whole triangle. For example, whilst 90 per cent. aqueous alcohol will dissolve up to four times its weight of benzene, it will only dissolve a third of its weight of hexane.

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CLIII.—*The Catalytic Action of Iodine in Sulphonation. Part I.*

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THE present investigation was undertaken with the view of ascertaining whether the addition of a trace of iodine to sulphuric acid (D 1·84) facilitates the sulphonation of aromatic compounds (compare Heinemann, Brit. Pat. 12260 of 1915). It has been found that ordinary sulphuric acid and a trace of iodine can advantageously be used in place of fuming sulphuric acid with or without the addition of phosphoric oxide, etc. The nature of the product is changed in certain cases, thus making easy the preparation of some of the acids difficult to obtain. The catalytic sulphonation is facilitated by the presence of an amino-, hydroxy-, or halogen group in the molecule, but proceeds with less ease in the case of carboxylic acids, and is inhibited in the case of nitro-compounds. This fact probably explains the non-formation of disulphonic acids in the product. It is significant that there is an optimum temperature for each reaction in which maximum transformation takes place. It has also been noticed that there is some liberation of iodine vapour, but no trace of sulphur dioxide or hydrogen iodide could be detected in the space above the reaction mixture.

The discrepancy between the actual yield and that theoretically possible was accounted for in nearly all cases by the unchanged original material.

EXPERIMENTAL.

In the experiments to be described below, the general method of work was to heat a mixture of a few grams of the substance and the calculated quantity, or an excess, of sulphuric acid (D 1·84), together with a trace of iodine, for a few hours at the temperature, determined by trial, at which the transformation was greatest. The product was poured into water, the free sulphuric acid removed with barium carbonate or hydroxide, and the acid liberated from the filtrate by exactly neutralising with sulphuric acid. The solution of the free acid was concentrated, whereupon it was obtained in a crystalline condition. In some cases the product was poured into a saturated solution of potassium chloride, when the potassium salt separated in fine crystals (*o*-nitrophenol, etc.). The acid or the potassium salt was converted by the usual method into the sulphonyl chloride,

from which the amide, mercaptan, etc., were prepared in order to characterise it. Some of the sulphonic acids described gave colour reactions with ferric chloride and characteristic salts with heavy metals. When the acid could not be satisfactorily identified, it was transformed through its amino- or nitro-groups, etc., into the corresponding hydroxy- or amido-compounds, etc., in order to establish its constitution. In some cases it was found convenient to extract the sulphonic acid from the sulphonated mass with alcohol (*o*-toluidine).

The results obtained from the fusion of the products with potassium hydroxide were not taken into account unless substantiated by further evidence.

Sulphonation of Benzoic Acid.

A mixture of 12 grams of benzoic acid, 9 c.c. of sulphuric acid, and a small crystal of iodine was heated at 175—180° for about six hours, at the end of which time no free benzoic acid separated on diluting a sample. The liquid, after cooling, was poured into water, when a clear solution was obtained. The solution was neutralised with barium carbonate, the precipitated barium sulphate filtered off, and the filtrate exactly neutralised with dilute sulphuric acid. After filtering, the liquid was concentrated to a syrup, and, on keeping in a desiccator, crystals were obtained, which were drained, washed with a small quantity of alcohol, and dried over sulphuric acid in a vacuum. The anhydrous crystals melted at 134—135° (uncorr.), and were very hygroscopic.

A test experiment was conducted side by side with the above in which no iodine was used; almost the whole of the benzoic acid was recovered unchanged.

The crystals in aqueous solution gave a reddish-brown coloration with ferric chloride, but no precipitate, and were identified as *o*-sulphobenzoic acid by the formation of salicylic acid when fused with potassium hydroxide at a moderately low temperature (Found: S = 15·0. Calc. for acid + $1H_2O$: S = 14·57 per cent.).

In the above experiment, about a gram of benzoic acid sublimed away, and was thus not sulphonated.

The following table gives a résumé of the results obtained with other substances:

Substance.	Products by known methods.	By the present method.	Yield. Per cent.	Optimum temperature.	Time of reaction Hours.
Toluene	*o*- and *p*-acids	*p*-acid only	90–95	100°	1
Benzoic acid	*m*- and *p*-acids	*o*-acid	Above 95	175–190	6
Phthalic acid	—	no product	—	—	—
Catechol	3-acid	4-acid	75	50–55	1½
Quinol	mono- and di-sulphonic acids	mono-acid	73	70	4
o-Nitrophenol.....	*p*-acid	*p*-acid	70	120	5
p-Nitrophenol	*o*-acid	*o*-acid	50	100–105	5
Nitrobenzene	—	no product	—	—	—
m-Dinitrobenzene ..	—	no product	—	—	—
o-Nitrotoluene	*p*-acid	*p*-acid	70	150	5
p-Nitrotoluene	*o*-acid	*o*-acid	5	140	4
o-Nitroaniline.....	*p*-acid	*p*-acid	60	125	4½
p-Nitroaniline	*o*-acid	*o*-acid	50	140	3
3-Nitroaniline	6-acid	6-acid	10	150	4½
o-Toluidine	5-acid	5-acid	60–65	150	3
p-Toluidine.....	—	no product	—	—	—
Chlorobenzene	*o*- and *p*-acid	*p*-acid	85	110	1½
Bromobenzene	*o*- and *p*-acid	*p*-acid	85	100	2

Summary and Conclusions.

(1) Iodine acts as a positive catalyst in sulphonation.

(2) Catalysis takes place smoothly when hydroxy-, amino-, chloro-, bromo-, or carboxy-groups are contained in the molecule, but with difficulty, or not at all, with nitro- or sulphonic substituents.

(3) There is an optimum temperature for each substance when the maximum transformation takes place.

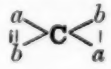
We have much pleasure in according our best thanks to Sir P. C. Rây for the interest he has taken in the work.

COLLEGE OF SCIENCE,
UNIVERSITY OF CALCUTTA. [*Received, January 28th*, 1920.]

CLIV.—*The Resolution of the Keto-dilactone of Benzophenone-2 : 4 : 2′ : 4′-tetracarboxylic Acid.*

By WILLIAM HOBSON MILLS and CHARLES REYNOLDS NODDER.

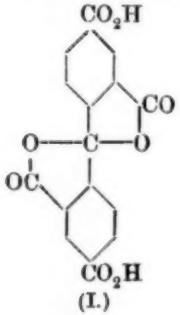
IT follows from the theory of the tetrahedral distribution of the four valencies of the carbon atom that a *spiro*cyclic compound of the type



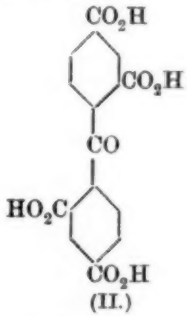
should exist in two enantiomorphous forms.

Previous attempts to obtain experimental confirmation of the molecular asymmetry of such compounds by resolution into optically active antipodes have, however, been unsuccessful (Marckwald, *Ber.*, 1906, **39**, 1176; Leuchs and various pupils, *Ber.*, 1912, **45**, 189, 2114; 1913, **46**, 2420), although Leuchs and Gieseler were able to obtain bis-δ-bromo-γ-valerolactone-αα-spirane, which contains only two asymmetric carbon atoms, in three inactive modifications, and they attributed the existence of the third form to the presence of a third centre of asymmetry in the substance, due to its *spiro*cyclic configuration.

A *spiro*cyclic compound of the type in question which appeared specially suitable for investigation is the keto-dilactone (I) of benzophenone-2:4:2′:4′-tetracarboxylic acid (II).



(I.)



(II.)

This compound was prepared by one of us (*Proc. Camb. Phil. Soc.*, 1915, **18**, 149) from di-*m*-xylyl ketone by oxidation to benzophenonetetracarboxylic acid, and dehydration of the latter by heating with hydrochloric acid. The method of synthesis, together with the fact that the product possesses the correct molecular weight, as we have found by the ebullioscopic method in acetone solution, leaves no doubt that it possesses the structure represented above.

After unsuccessful attempts with the commoner alkaloids, we have succeeded in resolving this substance into two optically active modifications with specific rotations $[\alpha]_D$ of approximately ±17° by means of a synthetic optically active base, α-phenylethylamine (Hunter and Kipping, T., 1903, **83**, 1147; Lovén, *J. pr. Chem.*, 1905, [ii], **72**, 307). Using the *d*-base, the *l*-acid was obtained, and the *d*-acid was isolated from the filtrate with the aid of the *l*-base.

The l-*Keto-dilactonic Acid.*—The following experiment is described as an example of several which have been carried out with similar results. The keto-dilactonic acid (5·75 grams) was suspended in methyl alcohol (100 c.c.), and a solution of *d*-α-phenylethylamine (4·09 grams), having $[\alpha]_D^{21}$ 39·64°, in methyl

alcohol (12 c.c.) was added drop by drop. The temperature rose from 22° to 26°, and a clear solution was obtained after the addition of about two-thirds of the base. After all the base had been introduced, dry ether (110 c.c.) was added. The salt rapidly crystallised, crystallisation being assisted by rubbing with a glass rod. The crop thus obtained (about 7 grams) was recrystallised from a mixture of methyl alcohol (210 c.c.) and ether (330 c.c.). The recrystallised salt (about 2 grams) was decomposed by treatment with hydrochloric acid (D 1·08), and the liberated keto-dilactonic acid carefully washed with water and dried. It was dissolved in methyl ethyl ketone, in which it is more readily soluble than in the other common solvents, and polarimetrically examined; 1·0375 grams in 30 c.c. gave α_D^{20} −2·25° (l=4), whence $[\alpha]_D^{20}$ −16·3°.

Of this product, 0·943 gram was combined, as before, with 0·671 gram of *d*-base. About 1 gram of salt was obtained, which, on decomposition, gave 0·6127 gram of acid. This was polarimetrically examined: 0·6127 in 13·1 c.c. gave $\alpha_D^{22·5}$ −1·58° (l=2), whence $[\alpha]_D^{22·5}$ −16·9°. The *l*-keto-dilactonic acid was recovered from solution and analysed (Found: C=59·4; H=2·44. $C_{17}H_8O_8$ requires C=59·99; H=2·37 per cent.).

The highest specific rotation which we have observed for the *l*-acid in the experiments which we have carried out up to the present is $[\alpha]_D^{20}$ −17·4° in methyl ethyl ketone solution.

The d-*Keto-lactonic Acid.*—The filtrate from which, as described above, the first crop of *d*-base–*l*-acid salt had been deposited gave, on acidification, 1·3 grams of an acid, which proved to be dextrorotatory; 0·679 gram in 30 c.c. of methyl ethyl ketone gave α_D^{21} 0·71° (l=4), whence $[\alpha]_D^{21}$ 7·9°. This acid was then combined with *l*-α-phenylethylamine, having $[\alpha]_D^{21}$ −38·5°, in the following manner. The acid (1·23 grams) was suspended in methyl alcohol (10 c.c.), *l*-base (0·87 gram) dissolved in methyl alcohol (2 c.c.) was added, and the salt precipitated with dry ether (6 c.c.). The acid (0·6585 gram) liberated from this salt was again combined with *l*-base (0·47 gram). The salt thus obtained gave, on decomposition, 0·559 gram of acid, which was polarimetrically examined; 0·559 gram in 13·1 c.c. gave α_D^{19} 1·50° (l=2), whence $[\alpha]_D^{19}$ 17·5°. From this acid, by repeating the above process, 0·426 gram of acid was obtained, on which the following observation was made: 0·426 gram in 13·1 c.c. of methyl ethyl ketone gave α_D^{19} 1·11°, whence $[\alpha]_D^{19}$ 17·1°. This acid was then recovered from solution and analysed (Found: C=59·70; H=2·38. $C_{17}H_8O_8$ requires C=59·99; H=2·37 per cent.).

The optically active forms of the keto-dilactonic acid are con-

siderably more readily soluble than the racemic form in all solvents examined. When saturated solutions of the *d*- and *l*-modifications in methyl ethyl ketone are mixed, an immediate, copious precipitate of the racemic form is produced.

To show the dependence of the optical activity on the lactonic structure of the compound, a solution of the *d*-acid in approximately 1 per cent. sodium hydrogen carbonate was examined in the polarimeter. The rotation was observed to diminish gradually, sinking to the half value in about twenty-four hours, and disappearing completely in about four days.

Further experiments on larger quantities of material are in progress in order to extend these observations, and particularly to determine the specific rotation of the optically pure acids.

One of us (C.R.N.) is indebted to the Department of Scientific and Industrial Research for a grant, for which he desires to express his thanks.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, November 2nd,* 1920.]

CLV.—*The Preparation and Physical Properties of Carbonyl Chloride.*

By RALPH HALL ATKINSON, CHARLES THOMAS HEYCOCK, and WILLIAM JACKSON POPE.

ALTHOUGH carbonyl chloride, $COCl_2$, was discovered by John Davy in 1812 (*Phil. Trans.*, 1812, **102**, 144), and has found extensive scientific and technical applications, very little information is contained in the literature concerning its preparation and physical properties; Davy obtained the substance by effecting the combination of carbonic oxide and chlorine under the influence of sunlight, and this method of preparation was elaborated by Wilm and Wischin (*Annalen*, 1868, **147**, 150). Schutzenberger (*Bull. Soc. chim.*, 1869, [ii], **12**, 198) and Armstrong (*Proc. Roy. Soc.*, 1870, **18**, 504) prepared it by the action of sulphur trioxide on carbon tetrachloride; the latter method has been recently studied by Grignard and Urbain (*Compt. rend.*, 1919, **169**, 17), and used by Paternò and Mazzucchelli (*Gazzetta*, 1920, **50**, i, 30) in their determination of the physical properties of carbonyl chloride.

On the introduction of carbonyl chloride as a weapon of chemical

warfare, it became necessary to ascertain which method of preparation was most adaptable as a works process for manufacture, and one described by Paternò (*Gazzetta*, 1878, **8**, 233) presented itself as probably the best for this purpose. Paternò states that, on passing a rapid current of mixed carbonic oxide and chlorine at the ordinary temperature over animal charcoal, carbonyl chloride is produced very rapidly, with considerable evolution of heat.

Difficulties were encountered in carrying out the Paternò method of preparation; a number of samples of commercial animal and vegetable charcoals proved almost without effect as catalysts. Ultimately, a charcoal was prepared which gave quite remarkable results in inducing the combination of carbonic oxide and chlorine; this was made in the following manner. Fresh ox bones were crushed, embedded in sand in a clay crucible, and burnt in a muffle furnace; the residual charcoal was then well extracted with hot hydrochloric acid, washed with water, and heated, as before, in sand. Finally, the bone charcoal was kept at a red heat for some time in a current of dry chlorine.

The charcoal prepared in this way was crushed into small fragments, and, after sifting off the dust, 10 grams were filled into a U-tube immersed in a water-bath; a rapid current of mixed carbonic oxide and chlorine, in which the former was in rather the greater volume, was then passed over the charcoal. Carbonyl chloride was produced freely when the water-jacket was kept at the ordinary temperature, but, on raising the bath temperature to between 40° and 50°, combination proceeded at a greater rate than that at which it was possible to supply the mixed gases. Using the bone charcoal catalyst in the manner described, and liquefying the carbonyl chloride by means of a freezing mixture, about 10 kilograms of the compound were produced without any sign that the activity of the 10 grams of charcoal had suffered diminution.

It is thus shown that Paternò's method for preparing phosgene is correctly stated, but that certain precautions are necessary in the preparation of the animal charcoal used. Further investigations showed that certain kinds of vegetable charcoal act even more vigorously in inducing the condensation of carbonic oxide and chlorine, and the highly activated wood charcoal used in the Army box respirator proved more efficient as a catalyst than the bone charcoal described above. A U-tube containing 10 grams of the box-respirator charcoal, which had been heated in a current of chlorine gas, proved extremely efficient when the water-jacket was maintained at 14°, and one such tube kept at this temperature yielded more than 20 kilograms of carbonyl chloride, with no sign that the catalytic activity had diminished. In the work

subsequently described in this paper, this active vegetable charcoal was used.

The carbonic oxide required for laboratory work on the preparation of carbonyl chloride is conveniently prepared by passing carbon dioxide over red-hot coke contained in iron tubes heated in an ordinary combustion furnace; the resultant gas, after passing over slaked lime and drying over sulphuric acid, is practically pure carbonic oxide. In industrial operations, it is to be expected, however, that the available carbonic oxide will contain hydrogen. It thus becomes of importance to compare the reactivity of carbonic oxide and hydrogen with chlorine under the catalytic influence of charcoal.

A series of experiments was therefore arranged in which varying proportions of hydrogen were mixed with the carbonic oxide and chlorine passed over the catalyst. It was found that the vegetable charcoal was so active at 14° in inducing the combination of carbonic oxide and chlorine that no advantage accrued from heating it to 90°, and that, working at temperatures below 70°, no hydrogen chloride was produced; at 80°, a small proportion of hydrogen chloride was formed, and this was greatly increased at 90°. It is thus shown that an active form of charcoal will effect the complete conversion of a mixture of carbonic oxide and chlorine into carbonyl chloride at a temperature 50° below that at which it begins to exhibit catalytic activity towards a mixture of hydrogen and chlorine. This conclusion seems of importance in connexion with the manufacture of carbonyl chloride from carbonic oxide containing hydrogen.

Carbonyl chloride dissociates into carbonic oxide and chlorine at moderately high temperatures; Bodenstein and Dunant (*Zeitsch. physikal. Chem.*, 1908, **61**, 437) state that under atmospheric pressure carbonyl chloride dissociates to the extent of 67, 80, and 91 per cent. at 503°, 553°, and 603°, respectively, and that dissociation is complete at 800°. The results obtained by these observers indicate that carbonyl chloride is appreciably dissociated at 300°.

A little consideration will show that if carbonyl chloride free from chlorine is to be manufactured from a mixture of carbonic oxide and chlorine containing an excess by volume of the former, the temperature of the catalyst must be maintained below that at which carbonyl chloride suffers appreciable dissociation. Further, it may be anticipated that, within the dissociation range of temperature, the catalyst will act comparatively sluggishly; the chlorine content of the produced carbonyl chloride should thus be higher than that indicated by the equilibrium composition, and the

catalyst would become feebler with prolonged use. The following experiments were made for the purpose of further elucidating this question.

A mixture of chlorine and carbon monoxide, containing 2·5 per cent. excess by volume of the latter and standing over brine saturated with chlorine, was dried over sulphuric acid and calcium chloride and passed over the absorbent charcoal, the latter being contained in a glass tube 45 cm. in length and 1·9 cm. in diameter, at different temperatures. For temperatures from 20° to 150°, the tube was heated in an oil-bath; for temperatures from 150° to 520° the tube was wrapped in three layers of copper gauze, encased in heavy iron gas pipe, and heated in a gas furnace, the gas pressure being carefully regulated. A quill tube was fitted into the axis of the catalyser tube, so that the temperature at any point could be measured by a copper–constantan thermo-couple. Control experiments showed that, on sliding the thermo-couple along the tube, the maximum temperature variation from place to place and for a period of several hours was not more than 10° when no chemical action was occurring. With this arrangement of apparatus, it proved easy to obtain carbonyl chloride free from chlorine at temperatures between 50° and 200°, and to collect 90 to 97 per cent. of the theoretical yield of phosgene. The important point was established, however, that the major part of the combination took place at the position in the tube first exposed to contact of the mixed gases. This was further demonstrated by keeping the first, or entrance, half of the tube at 18°, and the second, or exit, half of the tube at 100°; the main disengagement of heat occurred at the junction between the cool and the hot charcoal. By sliding the thermo-couple along the tube, the heating effect of the reaction could be followed as the couple was passed along the tube from the front of the exit half to the front of the entrance half.

It would be expected that, on subjecting mixtures of carbon monoxide and chlorine to the action of the catalyst, a certain maximum temperature would be attained which could not be exceeded—the equilibrium temperature at which the reverse action absorbed the heat liberated. On passing the mixed gases at the rates of 0·84 and 2·4 litres per minute, the temperature of 464° was attained, and remained constant; this is to be regarded as the maximum temperature which can be attained in the large-scale catalysing vessels used in the manufacture of carbonyl chloride. In the experiments just described, it is noteworthy that at the rate of flow of 0·84 litre per minute, the layer of charcoal found to be at 464° was only about 3 mm. long, whilst when the gas

passed through at 2·4 litres per minute, the layer of catalyst maintained at 464° was some 10 mm. in thickness. Attempts to prepare carbonyl bromide with the aid of charcoal as a catalyst were unsuccessful.

The Dissociation of Carbonyl Chloride.

Since the combination of carbon monoxide and chlorine is highly exothermic, $CO + Cl_2 = COCl_2 + 26C$, and the catalyst used is very active, it seemed undesirable to attempt the investigation of the dissociation curve of carbonyl chloride by the study of the association; the foregoing experiments have shown the difficulty of maintaining the catalyst at an even temperature during the formation of the chloride. A series of experiments was therefore made on the dissociation of carbonyl chloride for the purpose of determining the equilibrium between it and its dissociation products with temperature at the atmospheric pressure. Since the dissociation is endothermic and must proceed to equilibrium in contact with the catalyst, it should be possible to ensure that the catalyst will be kept at an even temperature, and will set up equilibrium at that temperature.

The carbonyl chloride used in all the further work described below was prepared from carbon monoxide and chlorine, and preserved in glass vessels in contact with mercury to ensure its freedom from chlorine.

The absorbent charcoal was maintained at a constant temperature, as described above, and a slow, steady stream of dry carbonyl chloride was passed over it. The gaseous products were passed through a separating funnel, *A*, of 338 c.c. capacity, entering at the bottom and leaving through a side-arm in the shoulder; when all the air had been displaced from *A*, the two taps were closed and a 20 per cent. potassium iodide solution was run in from a dropping funnel, *B*, stoppered into the neck of *A*. After well shaking the whole apparatus, further quantities of potassium iodide solution were run in until action was at an end. The solution was then washed out with water and the iodine titrated against thiosulphate in order to determine the free chlorine present in the gas. The residual gas, consisting of carbon monoxide with some carbonyl chloride and usually a little air, was passed into a gas pipette and shaken with sodium hydroxide solution to remove the chloride. The carbon monoxide was determined by absorption in a hydrochloric acid solution of cuprous chloride; the residual air was measured, and its volume deducted from the volume of the cylinder, *A*. Direct determinations of the chlorine, carbon monoxide, and

carbonyl chloride are thus obtained; the volumes of carbon monoxide and chlorine always corresponded closely, and in table I, which summarises the results, the mean of the two slightly differing volumes is given.

The degree of dissociation, D, of the carbonyl chloride is calculated from the formula

$$D = \frac{100 \times \text{Volume of } Cl_2}{\text{Volume of } COCl_2 + Cl_2},$$

and the curve (Fig. 1) is drawn by plotting the values of D against the temperature.

TABLE I.

Dissociation of Carbonyl Chloride.

		Percentage by weight.			Volume per cent.		Degree of dissociation,
	T°.	$COCl_2$.	Cl_2.	CO.	$COCl_2$.	CO & Cl_2.	D.
1.....	101	99·54	0·32	0·13	99·10	0·45	0·45
2.....	102	99·50	0·36	0·14	99·01	0·50	0·50
3.....	151	99·50	0·36	0·14	99·01	0·50	0·50
4.....	153	99·46	0·38	0·15	99·95	0·53	0·53
5.....	208	99·16	0·60	0·24	98·36	0·82	0·83
6.....	211	99·26	0·53	0·21	98·55	0·73	0·74
7.....	237	98·68	0·94	0·37	97·41	1·30	1·32
8.....	239·5	98·86	0·82	0·33	97·74	1·13	1·14
9.....	309	94·38	4·02	1·59	89·38	5·31	5·61
10.....	314	94·51	3·94	1·55	89·61	5·20	5·48
11.....	318	94·37	4·03	1·59	89·34	5·33	5·63
12.....	341	92·48	5·38	2·14	68·05	6·98	7·50
13.....	400	78·62	15·34	6·04	64·79	17·60	21·36
14.....	406	82·56	12·50	4·94	70·31	14·84	17·43
15.....	443	68·89	22·31	8·80	52·57	23·71	31·08
16.....	449	66·60	23·90	9·40	49·23	25·39	34·02
17.....	460	64·05	25·78	10·17	47·14	26·43	35·92
18.....	486	58·32	29·89	11·79	41·19	29·41	41·65
19.....	505	66·51	24·02	9·47	49·85	25·08	33·47
20.....	505	46·77	38·17	15·05	30·55	34·72	53·19
21.....	506	72·48	19·74	7·78	56·87	21·57	27·50
22.....	517	70·54	21·13	8·33	54·51	22·75	29·45

The method of experimentation which has been applied has the fault that it does not ensure the dissociation products being cooled so rapidly that their partial recombination is prevented. The effect of this is seen in the fact that certain points, namely, those from experiments numbered 19, 21, and 22, lie off the general course of the graph; in these experiments, the gas current was passed much more slowly than in the others. In consequence, it may be found later that the degree of dissociation for any particular temperature, as now recorded, is too low.

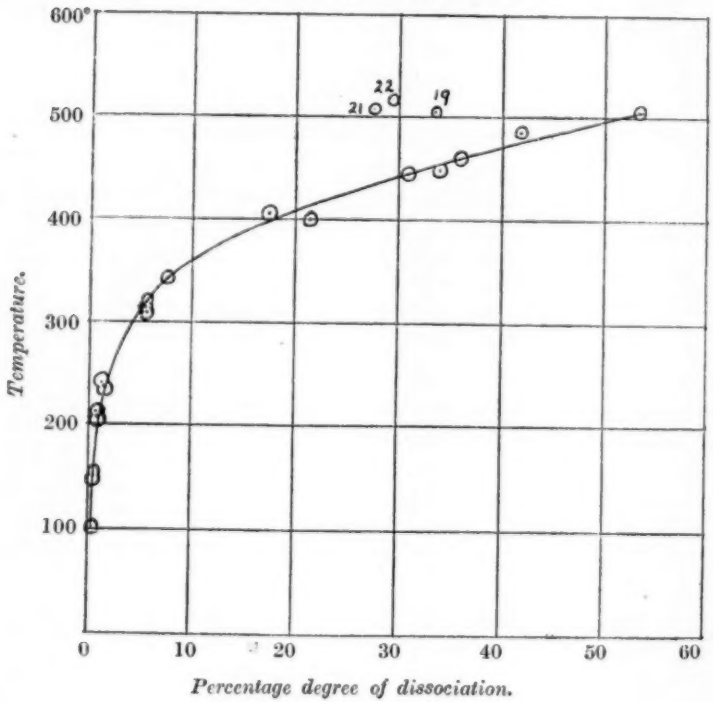
For practical purposes, it may be concluded that experiments 1 to 4, referring to temperatures of 100° to 150°, have given

identical results; the results of experiments 5 and 6, made at temperatures just above 200°, show a distinct increase in the degree of dissociation indicated at 100° and 150°. This increase is still more marked at 237° and 239°.

The accuracy of the suggestion made above, that carbonyl chloride free from chlorine can only be produced at temperatures

FIG. 1.

Dissociation of carbonyl chloride.



below 200°, must be regarded as fully substantiated by the above experimental results.

It is noteworthy that dissociation is indicated as occurring, even at 100° and 150°, by the results now recorded. It will be seen, however, that no difference is observable between the degree of dissociation indicated at 100° and 150°; the indication may therefore be attributed to some other cause than that of dissociation, possibly to the slight reaction between potassium iodide in the acid solution and carbonyl chloride referred to below. Such a reaction would not disturb the equal volume ratio found between

the carbon monoxide and chlorine, and it is recorded by Besson (*Compt. rend.*, 1896, **122**, 140) that carbonyl chloride dissolves hydriodic acid, with liberation of iodine.

Whilst Bodenstein and Dunant (*loc. cit.*) found that carbonyl chloride is dissociated to the extent of 67 per cent. at 503°, the smoothed curve (Fig. 1) expressing the Cambridge results indicates the dissociation to be 55 to 56 per cent. at this temperature. The former workers analysed the mixture of gases by bubbling it through aqueous potassium iodide solution, and it is known that pure carbonyl chloride liberates a small amount of iodine in such a solution, and that the quantity of iodine formed increases on keeping (Delépine and Ville, *Bull. Soc. chim.*, 1920, [iv], **27**, 283). It is significant that Bodenstein and Dunant obtained higher values for the dissociation in those experiments which lasted the longest (45, 80, and 120 minutes), and that the dissociation-temperature curve plotted from their results slopes at an improbable angle. The heat of formation of gaseous carbonyl chloride, calculated from the degree of dissociation, is +25·4 C. at 475° and +23·4 C. at 425°, according to the Cambridge results, and +19·2 C. at 528° and +26·6 C. at 578°, calculated from the results of Bodenstein and Dunant. Thomsen ("Thermochemische Untersuchungen," 1882, II, 364; *Ber.*, 1883, **16**, 2619) gives the value +26·14 C. at the ordinary temperature, and criticises adversely the value +18·8 C. previously obtained by Berthelot.

Vapour Pressure of Carbonyl Chloride between −100° *and* +100°.

The boiling point of carbonyl chloride is given by Beckmann (*Zeitsch. anorg. Chem.*, 1907, **55**, 370) as 8·2°/756 mm.; no other data concerning the vapour pressure of this compound were available before the recent publication of Paternò and Mazzucchelli (*loc. cit.*), who made a series of determinations at temperatures between −19° and +24°. We have determined the vapour pressure at temperatures from −183° to +18° in one type of apparatus, and by means of another have extended the results up to +100°.

The apparatus used in the determination of the vapour pressure between −183° and +18° is depicted diagrammatically in Fig. 2. The distillation flask, *F*, of about 60 c.c. capacity, is connected with a differential manometer, *HB*, placed in front of a silvered mirror on which a millimetre scale is engraved, so as to avoid parallax. Through the neck of the flask passes a thistle funnel, *S*, for the purpose of sealing the leads of the thermo-couple air-tight by means of Faraday wax at the point where the bulb joins

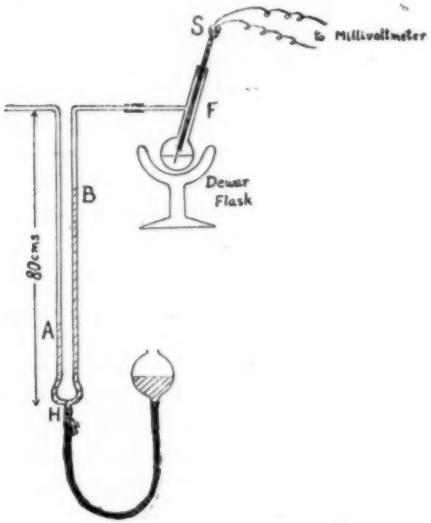
the stem. A joint thus made was found to be very satisfactory and quite unattacked by carbonyl chloride vapour.

The thermo-couple used was of copper–constantan; one junction was kept in ice and the other in the liquid carbonyl chloride. The couple was connected to a delicate millivoltmeter, which could be read with accuracy to 0·01 millivolt. For the graduation of the couple, the following temperatures were assumed:

TABLE II.

		Millivolts.
Steam at 760 mm. pressure	100°	+4·07
Melting ice	—	0·00
Freezing point of mercury	−39	−1·38
Solid carbon dioxide and ether	−79	−2·65
Boiling liquid oxygen	−183	−5·12

FIG. 2.



The millivolts corresponding with each of these temperatures were read off on the instrument, and the results plotted. The accuracy of the calibration was confirmed by determining with the aid of the couple the boiling point of a very pure sample of ethylene; this gave the value −104°, which compares well with the standard value of −103·5° given by Wroblewski and Witkowski.

After some preliminary trials, the following procedure was adopted. About 50 c.c. of pure liquid carbonyl chloride was distilled into the flask, *F*; the mercury was then run out of the mano-

meter, and the whole apparatus exhausted while the contents of the flask were maintained at −80°. The temperature of the carbonyl chloride was then allowed to rise until vapour was freely given off. This process was repeated several times during the three days occupied by the experiments, so as to ensure the complete absence of air.

A series of observations of the pressure and temperature of the carbonyl chloride was made at the selected temperatures, with the following results (table III):

TABLE III.

	Temperature.	Pressure mm. of Hg.
Water-bath	+100°	16·07×760
„ „	+50	5·11×760
„ „	+17·5	1105·5
Melting ice	—	568·3
Ice and salt mixture	−19	236·0
Freezing point of mercury	−39	89·5
Solid carbon dioxide and ether	−79	4·0
Boiling liquid oxygen	−183	0 mm.

These results have been plotted on the curve (Fig. 3), from which the vapour pressures of carbonyl chloride for each 10° between +20° and −100° have been taken; these values are included in table V.

After the vapour pressure of carbonyl chloride had been measured over the range −183° to +18°, recourse was had to a different form of apparatus in order to extend the observations up to 100°. A sealed tube containing carbonyl chloride and a special type of manometer was heated in a water-bath to the desired temperature, and kept there for two to three hours. The glass manometer is shown in Fig. 4. The graduated tube, *AB*, was carefully calibrated by means of mercury. At the same time, the volume of the manometer was measured by weighing the amount of mercury which it contained. After the manometer had been thoroughly cleaned, the tube, *AB*, was silvered internally. The slight difference in the weight of the manometer before and after silvering proved that the amount of silver deposited was so small that its effect could be neglected.

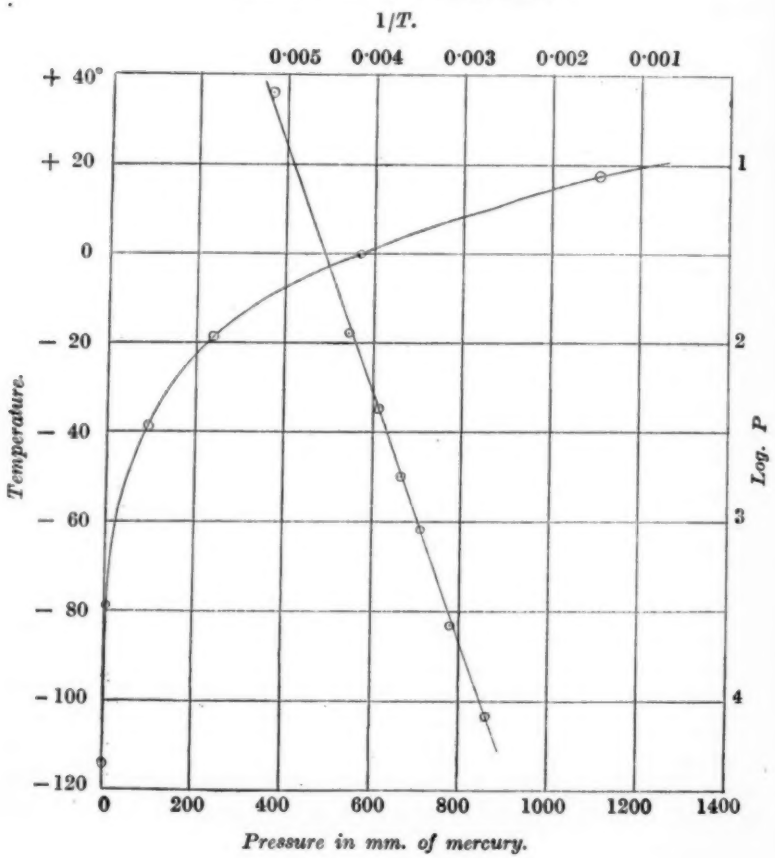
The manometer, having been carefully cleaned and dried, was filled with dry air and lowered into a hard glass tube containing about 10 c.c. of dry mercury (see Fig. 5). A wire, *W*, served to keep the manometer upright in the centre of the tube. The tube was drawn off, and finally sealed after 30 c.c. of pure liquid carbonyl chloride had been introduced in the usual manner; due care was taken to ensure that the space above the liquid contained

carbonyl chloride vapour only, and that air was absent. The pressure tube, placed inside an iron tube, was kept at 50° for two hours in a water-bath.

As the pressure of the vapour increases, it forces the mercury into the manometer, thereby compressing the air. When the

FIG. 3.

Vapour pressure of carbonyl chloride.



mercury rises into the silvered part of the tube, it dissolves the silver as far as the highest point it reaches. Thus a record is made of the volume of the compressed air at the temperature of the experiment.

After the tube had cooled and a note been made of the point to which the mercury had dissolved the silver, the experiment was

repeated at 100°. The following data were obtained: volume of manometer, 4·675 c.c.; barometer, 758 mm.; temperature, 16·6°. Volume of compressed air at 50° = 1·038 c.c., and at 100° = 0·380 c.c. The following results were calculated after applying corrections for the pressure of the columns of carbonyl chloride and mercury:

Vapour pressure of carbonyl chloride at 50° = 5·11 × 760 mm.
" " " " 100° = 16·07 × 760 mm.

It was noticed that the surface of the mercury was slightly dirty

FIG. 4.

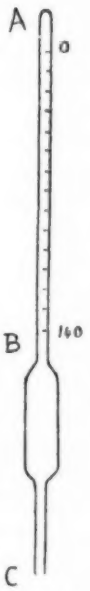


FIG. 5.

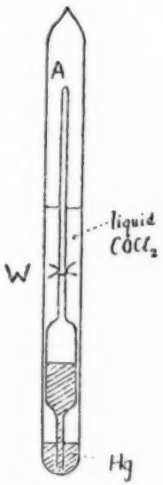
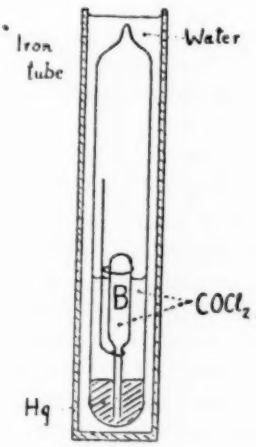


FIG. 6.



after these experiments; it is suggested that some chemical change occurs in accordance with the equation

$$2Hg + COCl_2 = CO + Hg_2Cl_2,$$

and that the two values last given may be rather high by reason of the formation of a trace of carbonic oxide.

From the vapour-pressure determinations now recorded, the molecular heat of evaporation (without performance of external work) of carbonyl chloride between 0° and 8° is calculated as approximately 5500 calories. A molecular heat of evaporation of 5500 calories for carbonyl chloride gives a value of 28° to 29° for the molecular rise in boiling point of this solvent; Beckmann (*Zeitsch. anorg. Chem.*, 1907, **55**, 371) has determined this

quantity experimentally as 29°. Since the latter value is obtained as the mean of six values lying between 27·2° and 30·8°, the agreement between his value and ours may be considered satisfactory.

Our values for the vapour pressure of carbonyl chloride at the higher temperature are rather higher than the Italian ones, whilst at 0° and below the reverse is the case. That our values are concordant among themselves is seen from the fact that the curve plotted between the reciprocal of the absolute temperature and the logarithm of the observed vapour pressure is practically a straight line; this curve is, indeed, drawn as a straight line in Fig. 3.

Since the vapour-pressure curve for carbonyl chloride only begins to fall rapidly at below −40°, it is clear that considerable losses will occur in the preparation unless the effluent gas saturated with carbonyl chloride is cooled well below −40°. The solubility of the chloride in a number of liquids, from which it might be subsequently recovered by evaporation, was therefore ascertained in order to learn whether washing the effluent gas with a solvent would lead to economy.

Solubility of Carbonyl Chloride in Organic Liquids.

Two or three c.c. of the solvent to be used are placed in a glass bulb of about 10 c.c. capacity immersed in a constant-temperature bath, and a slow current of the gas evolved from gently boiling carbonyl chloride is passed through the bulb until no further absorption occurs. Saturation was generally complete in about three hours, and the contents of the bulb were then hermetically sealed. The weight of the saturated solution was given by direct weighing, and the quantity of carbonyl chloride present determined by breaking the bulb in a closed bottle containing 50 or 100 c.c. of standard sodium hydroxide solution and titrating with standard acid. The number of grams of carbonyl chloride dissolved by 100 grams of solvent are now stated.

Toluene.—At 17·0°, 23·5°, 30·5°, and 31·5°: 244·7, 124·2, 79·38, and 74·48 respectively.

Coal-tar Xylene.—At 12·3°, 16·4°, 16·9°, 23·8°, and 29·8°: 457·3, 225·6, 217·9, 103·4, and 71·24 respectively.

Creosote Oil.—At 16·2°: 77·42.

Petroleum boiling at 180—280°.—At 12·3°, 15·8°, 16·7°, 22·4°, 23·7°, 29·9°, and 30°: 263·8, 163·1, 143·4, 79·5, 71·2, 49·2, and 48·6 respectively.

Heavy Lubricating Oil.—At 15·6°, 23·5°, and 31·0°: 79·7, 39·3, and 24·5 respectively.

Nitrobenzene.—106·4 at 16·8°.

α-Chloronaphthalene.—104·5 at 17·0°.

Chlorobenzene.—At 12·3°, 16·6°, 16·7°, 24·2°, and 29·7°: 422·1, 204·3, 221·6, 99·9, and 81·9 respectively.

Acetylene Tetrachloride.—At 16·8°, 25·1°, and 29·9°: 149·7, 89·4, and 74·9 respectively.

The solubility of carbonyl chloride differs widely according to the solvent. Toluene, coal-tar xylene, and chlorobenzene are by far the best solvents of those examined, and in view of their elevated boiling points would appear to offer most advantages as scrubbing agents for effluent gases containing carbonyl chloride. Ordinary burning petroleum boiling at 180° to 280° is the next best solvent, and heavy mineral lubricating oil and acetylene tetrachloride are not quite so good.

Melting and Freezing Points of Carbonyl Chloride.

The only recorded melting point for carbonyl chloride is that given by Erdmann (*Annalen*, 1908, **362**, 148) as −118°. Our determinations were made by immersing the bare junction of a standardised copper–constantan thermo-couple in pure liquid carbonyl chloride; on cooling in a bath of liquid air, the carbonyl chloride solidified to a white, crystalline mass, and on allowing the temperature to rise slowly, the temperature, as recorded by a millivoltmeter, remained steady at −126° throughout the melting of the substance. On cooling the liquid very slowly, with constant shaking, the carbonyl chloride commenced to crystallise at −128°.

Density of Liquid Carbonyl Chloride.

The density of liquid carbonyl chloride was determined by Emmerling and Lengyel (*Annalen, Supp.*, 1870, **7**, 106) as 1·432 at 0°/4° and as 1·392 at 18·6°/4°; Paternò and Mazzucchelli (*loc. cit.*) have quite recently made a series of careful determinations between −15·4° and +59·9°. We have determined the density at −104·0°, −79°, 0°, and +49·9° with the aid of weight thermometers of transparent silica; two such thermometers, *A* and *B*, were used.

After filling the thermometers with mercury and repeatedly boiling out, they were cooled for some hours in ice, dried in a vacuum desiccator, and weighed, precautions being taken to collect the mercury overflow; thermometer *A* contained 80·1054 grams of mercury at 0°, whilst *B* contained 67·2640 grams. Assuming

Regnault's value of 13·5955 grams for the weight of 1 c.c. of mercury at 0°, the capacities of *A* and *B* are calculated as 5·8920 and 4·9475 c.c. respectively.

Thermometer *A* was filled with mercury at 0°, heated in a steam hypsometer (Bar. 768 mm.) for an hour, and then weighed; it contained 78·6835 grams of mercury at 100·3°. From these values, the coefficient of apparent expansion of mercury in silica is calculated as $(1·4219)/(78·6835 \times 100·3) = 0·000,180,17$; assuming Regnault's value of 0·000,180,92 for the coefficient of absolute expansion of mercury between 0° and 100°, the coefficient of cubic expansion of transparent silica becomes 0·000,000,75, a quantity which is small enough to be neglected.

In making the density determinations at 0° and lower temperatures, the thermometer *A* was filled with liquid carbonyl chloride in the ordinary way and kept at the steady, low temperature for for half to one hour; no attempt was made to weigh the vessel, on account of the difficulty of preventing moisture from the air condensing on it during transference. The weight of carbonyl chloride was found by removing the tube from the cooling bath and lowering it into a bottle containing 200 c.c. of ice-cold standard (2*N*) sodium hydroxide, which was then stoppered and clamped. The liquid in the thermometer slowly boiled off, usually taking from one to two hours, and when all had evaporated and reacted with the alkali, the excess of the latter was determined by titration with an acid; the weight of carbonyl chloride was then calculated.

In making the determination at +49·9°, the weight thermometer, *B*, was filled at −79°, and was then lowered, nose downwards, into a stout combustion tube, the lower end of which contained mercury. Cold carbonyl chloride was poured into the tube, which was then drawn off and placed inside an iron tube (see Fig. 6) gradually heated to 49·9° in a water-bath, and kept at that temperature for three hours. The tube was then slowly cooled, finally in ice and salt, and opened in the same way as in an ordinary pressure-tube experiment. The thermometer, which now contained mercury and carbonyl chloride, was withdrawn from the tube, drenched on the outside with cold ether, placed in the standard sodium hydroxide solution, and allowed to become warm slowly; the titration was then performed as before.

All errors due to the deformation of the silica tube by pressure were in this way eliminated, as the pressure within and without the tube was practically the same.

The density of carbonyl chloride (that is, weight in grams of 1 c.c.) was determined at −104° (boiling point of ethylene), −79° (solid carbon dioxide wetted with ether), 0° (ice), and +49·9°

(thermo-regulator); the results of the actual experiments are given in tabular form (table IV).

TABLE IV.

Temperature.	Weight thermometer.	Weight of $COCl_2$ in grams.	Density of $COCl_2$. (Weight of 1 c.c. of liquid.)
−104·0°	A (Vol. 5·892 c.c.)	9·892	1·679
−79	„	9·519	1·616
−79	„	9·503	1·613
0	„	8·463	1·436
0	„	8·443	1·433
+49·9	B (Vol. 4·948 c.c.)	6·502	1·314

From these results, a smooth curve was drawn, and a table (table V) constructed giving the density of carbonyl chloride for each 10° from −100° to +50°.

TABLE V.

Density and Vapour Pressure of Liquid Carbonyl Chloride.

Tempera-ture.	Density. Grams per c.c.	Vapour pressure. Mm. of mercury	Tempera-ture.	Density. Grams per c.c.	Vapour pressure. Mm. of mercury.
−110°	1·685	—	−20	1·481	226
−100	1·663	—	−10	1·459	361
−90	1·640	—	0	1·435	568
−80	1·617	4	+10	1·412	844
−70	1·594	11	+20	1·388	1212
−60	1·572	24	+30	1·363	—
−50	1·549	47·5	+40	1·338	—
−40	1·526	85	+50	1·314	5·11 × 760
−30	1·504	141			

The mean coefficient of cubical expansion of carbonyl chloride between −79° and +49·9° is calculated as

$$(1·6145 - 1·3140)/(1·3140 \times 129) = 0·001,77.$$

The values for the temperature ranges −104° to −79°, −79° to 0°, and 0° to +49·9° are 0·001,60, 0·001,59, and 0·001,84 respectively.

The values for the density of liquid carbonyl chloride which we now give are slightly higher than those obtained by the Italian workers; the latter obtained their product by the action of sulphur trioxide on carbon tetrachloride, and it is curious that Emmerling and Lengyel, who prepared their material, as we did, by the combination of carbonic oxide and chlorine, obtained results for the densities which are almost identical with ours for the two tempera-

tures at which they worked. The discrepancies between the results obtained by Paternò and Mazzucchelli and by ourselves may possibly be traced to the presence of some characteristic impurity in the carbonyl chloride made by one or the other method.

The work described in the present paper was carried out for the purposes of the Chemical Warfare Department, and permission for its publication has been given by the General Staff. Our thanks are due to our assistant, Mr. George Hall, for much help in experimental work.

THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE. [*Received, October 15th*, 1920.]

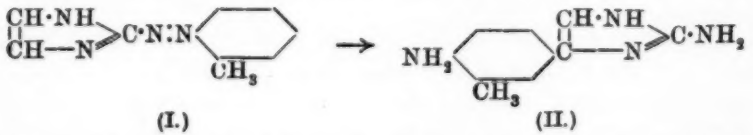
CLVI.—o- *and p-Tolueneazoglyoxalines.*

By FRANK LEE PYMAN and LEONARD ALLAN RAVALD.

IN continuation of previous work on arylazoglyoxalines (Fargher and Pyman, T., 1919, **115**, 217), the interaction of *o*- and *p*-toluenediazonium chlorides and glyoxaline has been studied. The methods employed and the products obtained are generally similar to those described in the previous communication.

o-Toluenediazonium chloride combines with glyoxaline in aqueous sodium carbonate, giving 2-o-*tolueneazoglyoxaline* (I) in poor yield, a considerable amount of bis-*o*-tolueneazo-*o*-cresol being produced as a by-product. On replacing the sodium carbonate by sodium hydroxide, the yield was very little better, but the by-products were of different character, whilst when sodium hydrogen carbonate was used in the place of sodium carbonate, bis-*o*-tolueneazo-*o*-cresol was again produced, but no tolueneazoglyoxaline.

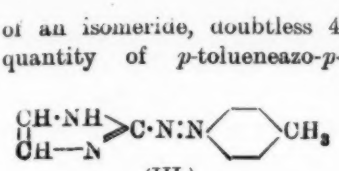
2-*o*-Tolueneazoglyoxaline resembles 2-benzeneazoglyoxaline closely in physical and chemical properties. On reduction with stannous chloride, it gives 2:4′-*diamino*-4-m-*tolylglyoxaline* (II).



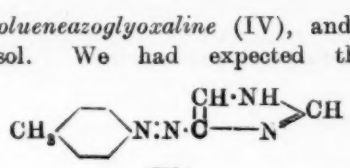
(I.) (II.)

The combination of *p*-toluenediazonium chloride with glyoxaline in aqueous sodium carbonate leads to the formation of 2-p-*tolueneazoglyoxaline* (III) in good yield, together with a small amount

of an isomeride, doubtless 4-p-*tolueneazoglyoxaline* (IV), and a quantity of *p*-tolueneazo-*p*-cresol. We had expected that



(III.)



(IV.)

2-*p*-tolueneazoglyoxaline would resemble 2-*p*-bromobenzeneazoglyoxaline in giving a good yield of 2-aminoglyoxaline when reduced with stannous chloride under the conditions employed by Fargher and Pyman (*loc. cit.*, p. 244), but this was not the case, 2-aminoglyoxaline being produced in a yield of less than 15 per cent. of the theoretical, together with *p*-toluidine, guanidine, ammonia, and unidentified products. When 2-*p*-tolueneazoglyoxaline is reduced with zinc dust and acetic acid under the conditions previously employed for the reduction of 2-benzeneazoglyoxaline (*ibid.*, p. 241), *p*-toluidine and glycocyamidine were obtained in yields amounting to 97 and 42 per cent. of the theoretical respectively.

Experimental.

2-o-*Tolueneazoglyoxaline*.

o-Toluidine (10·7 grams) was diazotised, and the product added to a solution of 6·8 grams of glyoxaline and 20 grams of anhydrous sodium carbonate in 500 c.c. of water at 5°. After keeping overnight, the brown deposit was collected and extracted with 5 per cent. hydrochloric acid. On the addition of sodium carbonate, the extract deposited 4·8 grams of crude 2-*o*-tolueneazoglyoxaline melting at 165°, the yield amounting to 26 per cent. of the theoretical. The material insoluble in dilute hydrochloric acid amounted to 7 grams and melted at 120°; after recrystallisation from alcohol, it gave 3·3 grams of pure bis-*o*-tolueneazo-*o*-cresol, which melted at 147° (corr.), and was identified by analysis [Found (mean): C=72·4; H=6·0; N=16·6. Calc.: C=72·2; H=6·1; N=16·9 per cent.] and by comparison with a specimen prepared by the action of *o*-toluenediazonium chloride on *o*-cresol (Noelting and Werner, *Ber.*, 1890, **23**, 3260).

2-o-*Tolueneazoglyoxaline* crystallises from alcohol in brownish-yellow crystals of indeterminate shape, which melt at 185—186° (corr.). It is very readily soluble in alcohol or chloroform, less readily so in ether or benzene (Found: C=64·6, 64·4; H=5·4, 5·7; N=30·1. $C_{10}H_{10}N_4$ requires C=64·5; H=5·4; N=30·1 per cent.).

Reduction of 2-o-*Tolueneazoglyoxaline with Stannous Chloride. Isolation of* 2:4′-*Diamino*-4-m-*tolylglyoxaline.*

Two grams of 2-*o*-tolueneazoglyoxaline were dissolved in 20 c.c. of hot 2·5 per cent. hydrochloric acid and mixed with 12 c.c. of stannous chloride (40 per cent. w/v) in hydrochloric acid. On cooling the solution and adding 20 c.c. of concentrated hydrochloric acid, 4 grams of a crystalline stannichloride were deposited, which, after the removal of the tin, gave 2 grams of 2:4′-diamino-4-*m*-tolylglyoxaline dihydrochloride, that is, 67 per cent. of the theoretical yield.

2:4′-*Diamino*-4-m-*tolylglyoxaline dihydrochloride* separates from dilute hydrochloric acid in microscopic needles, which form a white, spongy mass. After drying at 50°, it contains $1H_2O$. It is readily soluble in cold, very readily so in hot, water [Found (in substance dried at 50°): C=43·0; H=5·8; N=19·9, 20·1; Cl=25·7; H_2O=6·9. $C_{10}H_{12}N_4,2HCl,H_2O$ requires C=43·0; H=5·8; N=20·1; Cl=25·5; H_2O=6·5 per cent.].

Its reactions with potassium permanganate, sodium nitroprusside, sodium diazobenzene-*p*-sulphonate, and nitrous acid are similar to those of the lower homologue (T., 1919, **115**, 240). The base appears to be unstable, for, on the addition of ammonia to an aqueous solution of the dihydrochloride, a white, flocculent precipitate is formed, which rapidly darkens when separated from the solution.

The sparingly soluble *sulphate* separates as a mass of woolly needles on the addition of sulphuric acid to an aqueous solution of the salt.

The *dipicrate* separates as a crystalline powder, which melts at about 210° (corr.) after sintering earlier. It is sparingly soluble in boiling water.

2- *and* 4-p-*Tolueneazoglyoxalines.*

p-Toluidine (10·7 grams) was diazotised, and the product added to a solution of 6·8 grams of glyoxaline and 20 grams of anhydrous sodium carbonate in 500 c.c. of water at 5°. After keeping overnight, the yellowish-brown, insoluble product was collected and extracted with 5 per cent. hydrochloric acid. One gram of dark red, amorphous matter remained undissolved, and, on crystallisation from alcohol, yielded *p*-tolueneazo-*p*-cresol, which melted at 112° (corr.), and was identified by analysis (Found: C=73·7; H=6·8; N=12·5. Calc.: C=74·3; H=6·3; N=12·4 per cent.) and by comparison with a specimen prepared by the action of

p-toluenediazonium chloride on *p*-cresol (Noelting and Kohn, *Ber.*, 1884, **17**, 354). The hydrochloric acid extract was basified with sodium carbonate, and deposited 15·2 grams of the mixed toluene-azoglyoxalines melting at 220°, that is, 86 per cent. of the theoretical yield. On recrystallisation from alcohol, 11·6 grams of 2-*p*-tolueneazoglyoxaline were obtained in a pure state, and small crops of impure material. From the final filtrate, 4-*p*-tolueneazoglyoxaline was isolated in the form of its hydrochloride.

2-p-*Tolueneazoglyoxaline* crystallises from alcohol in yellow leaflets, which melt at 235° (corr.). It is soluble in boiling alcohol to the extent of rather less than 5 per cent. (Found: C=64·1, 64·4; H=5·6, 5·6; N=30·1. $C_{17}H_{10}N_4$ requires C=64·5; H=5·4; N=30·1 per cent.).

The hydrochloride was crystalline, but deliquescent.

4-p-*Tolueneazoglyoxaline*, prepared from the pure hydrochloride, crystallised from alcohol in yellow leaflets, which melted at 152° (corr.) (Found: C=63·9; H=5·5; N=31·0. $C_{10}H_{10}N_4$ requires C=64·5; H=5·4; N=30·1 per cent.).

The *hydrochloride* crystallises from dilute hydrochloric acid in fine, yellow needles forming a felted mass. The air-dried salt melts first at 76° (corr.), loses $2H_2O$ at about 117°, and melts again after darkening at 185° (corr.). It is very readily soluble in water [Found (in air-dried salt): Cl = 13·8; H_2O = 13·5. $C_{10}H_{10}N_4$,HCl,$2H_2O$ requires Cl=13·7; H_2O=13·9 per cent.].

We desire to thank the Salters' Institute of Industrial Chemistry for the grant of a fellowship, which has enabled one of us (L.A.R.) to take part in the investigation.

MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, October 16th*, 1920.]

CLVII.—*The Sulphonation of Glyoxalines.*

By FRANK LEE PYMAN and LEONARD ALLAN RAVALD.

DIRECT sulphonation of glyoxalines has not been effected previously, but in two cases derivatives of glyoxaline-2-sulphonic acid have been prepared indirectly. Thus, Anschütz (*Annalen*, 1895, **284**, 18) obtained 4:5-diphenylglyoxaline-2-sulphonic acid by the oxidation of 2-thiol-4:5-diphenylglyoxaline, whilst salts of caffeine-8-sulphonic

acid are formed by the action of hot aqueous sulphites on 8-chlorocaffeine (D.R.-P. 74045).

In view of the stability and pronounced aromatic character of glyoxaline, it seemed probable that this base, like pyrazole and pyridine, would be susceptible to direct sulphonation, and this has proved to be the case, a *glyoxalinesulphonic acid* being obtained in good yield under suitable conditions. Presumably, sulphonation takes place in the 4-position, as does nitration (Fargher and Pyman, T., 1919, **115**, 217; Fargher, this vol., p. 668), and the investigation will be continued and extended to alkylglyoxalines to elucidate this point.

Experimental.

Glyoxaline, in the form of its sulphate, was added to sulphuric acid or fuming sulphuric acid and the mixture heated. The diluted solution was treated with barium hydroxide and subsequently with carbon dioxide, evaporated to dryness, and extracted with chloroform. This removed the unchanged glyoxaline and left crude barium glyoxalinesulphonate.

The consequences of varying the conditions appear in the following table:

No. of experiment.	Proportion of glyoxaline (base) to fuming sulphuric acid.	Strength of fuming sulphuric acid in percentage of free sulphur trioxide.	Temperature.	Duration of heating (hours).	Yield of sulphonate. Percentage of theoretical.	Glyoxaline recovered. Per cent.
1	1 : 2	(98% H_2SO_4)	100°	3	Nil.	85
2	1 : 3	12	,,	,,	Nil.	74
3	,,	40	,,	,,	4	96
4	,,	,,	160	,,	18·5	57
5	,,	,,	,,	6	9	69
6	,,	,,	200	3	11	85
7	,,	,,	260	,,	2	46
8	,,	50—60	100	,,	20	46
9	,,	,,	160	,,	52	Trace.
10	,,	,,	,,	,,	55	26
11	1 : 4	,,	,,	,,	78	Trace.
12	,,	,,	,,	,,	70	,,
13	,,	,,	,,	,,	83	,,

The crude barium glyoxalinesulphonate crystallised almost completely on treatment with water. From the pure salt the free acid and the sodium and ammonium salts were prepared by treatment with the equivalent quantities of sulphuric acid and its salts.

Glyoxalinesulphonic acid crystallises from water in large, colourless cubes which are anhydrous. It begins to soften at 290° and is

entirely molten at 307° (corr.). It is soluble in about 5 parts of cold or 2 parts of hot water, but is almost insoluble in alcohol. (Found, C = 24·2; H = 2·6; N = 18·9. $C_3H_4O_3N_2S$ requires C = 24·3; H = 2·7; N = 18·9 per cent.)

Glyoxalinesulphonic acid is strongly acid to litmus, whilst its salts are only faintly alkaline. It does not combine with strong aqueous acids. On adding sodium diazobenzene-*p*-sulphonate to glyoxalinesulphonic acid in excess of aqueous sodium carbonate, no immediate coloration is produced, but a deep red colour develops in the course of a few minutes. In the presence of sodium hydroxide the solution remains pale yellow even on keeping. An attempt to nitrate glyoxalinesulphonic acid by boiling 1·1 grams with a mixture of 1 c.c. of fuming nitric acid and 1 c.c. of sulphuric acid was unsuccessful, the glyoxalinesulphonic acid being recovered unchanged.

The *barium* salt crystallises from water in colourless octahedra, which are anhydrous, soluble in 3 parts of hot water, and little less soluble in cold water, but insoluble in alcohol. (Found: Ba = 34·2. $(C_3H_3O_3N_2S)_2Ba$ requires Ba = 34·1 per cent.)

The *sodium* salt crystallises from water in large, colourless tablets, which contain $2H_2O$. It is very readily soluble in water, but almost insoluble in alcohol. (Found, in air-dried salt: Na = 11·2; H_2O = 17·7. $C_3H_3O_3N_2SNa,2H_2O$ requires Na = 11·2; H_2O = 17·5 per cent.)

The *ammonium* salt crystallises from water in large, colourless prisms. It is very readily soluble in water, and easily so in hot moist alcohol, but almost insoluble in absolute alcohol. It loses ammonia at temperatures above 100°, leaving the free acid. The air-dried salt lost 1·5 per cent. of water in a vacuum over sulphuric acid. (Found, in salt dried in a vacuum: N = 25·4; loss at 120° = 10·5. $C_3H_3O_3N_2S{\cdot}NH_4$ requires N = 25·4; loss of NH_3 = 10·3 per cent.)

We desire to thank the Salters' Institute of Industrial Chemistry for the grant of a fellowship which has enabled one of us (L. A. R.) to take part in the investigation.

MUNICIPAL COLLEGE OF TECHNOLOGY,
THE UNIVERSITY OF MANCHESTER. [*Received, October 16th*, 1920.]

CLVIII.—*The Velocity of Decomposition of High Explosives in a Vacuum. Part I.*

By Robert Crosbie Farmer.

Previous work on the stability of explosives has been devoted almost entirely to the nitric esters. The methods used depend for the most part on the detection and estimation of the oxides of nitrogen evolved on heating, and are not, in general, applicable to nitro-aromatic compounds or to mercuric fulminate, azides, etc. In order to meet the need for a simple quantitative stability test for such compounds, the vacuum test described below was developed. This has been widely used for high explosives, more particularly for trinitrophenylmethylnitroamine. It has proved itself so simple in use after some thousands of tests that it may be of interest for the investigation of other reactions in which gases are evolved. Some measurements of the rate of decomposition in a vacuum have been made on guncotton (Obermüller, *Mitt. Berl. Bezirksver.*, 1904, **1**, 30; Dupré, *Ann. Rep. Insp. of Explosives*, 1903, 26; 1904, 28; 1905, 29; Hodgkinson and Coote, *Chem. News*, 1905, **91**, 194; Robertson and Napper, T., 1907, **91**, 764; Willcox, *J. Amer. Chem. Soc.*, 1907, **30**, 271; Pleus, *Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1910, **5**, 121), on silver oxalate (Hoitsema, *Zeitsch. physikal. Chem.*, 1896, **21**, 137), trinitrotoluene (Verola, *Mém. poud. Salp.*, 1911—1912, **16**, 40), and tetryl (Knowles, *J. Ind. Eng. Chem.*, 1920, **12**, 246). The methods described were not, however, convenient as standard tests for high explosives.

From measurements on a large number of explosives, it appears that these are in all cases subject to a gradual decomposition, with evolution of gas, at temperatures below their ignition points. The velocity decreases strongly as the temperature is lowered, but there can be little doubt that a very slow decomposition must occur even at the ordinary temperature.

As in the case of nitric esters (Farmer, this vol., p. 811), the decomposition is partly catalytic and partly non-catalytic; when catalytic influences are eliminated, the velocity sinks to a minimum. In many cases, the catalytic decomposition outweighs the intrinsic decomposition of the pure substance, and it is frequently difficult to purify the explosive to such a degree that the catalytic influences are completely removed. For the same reason, different preparations of the same substance often differ considerably in their rates of decomposition. Frequently the evolution of gas proceeds

with an acceleration due to autocatalysis, whilst in other cases it becomes slower after a time, owing to the decomposition and consequent elimination of impurities. In many cases the presence of moisture gives rise to very erratic results, and special steps are therefore taken to eliminate this influence. As a rule, the decomposition has been carried only to the extent of a small evolution of gas. The measurement of small volumes of gas has, it is true, the disadvantage that the measurements are more affected by traces of volatile matter, etc., but if the decomposition is carried further, the products formed are liable to have a very disturbing effect, and frequently a very rapid evolution of gas sets in.

The nitro-aromatic compounds are, in general, very much more stable than the nitric ester explosives. Whilst guncotton shows a marked decomposition in Will's test at 135° in four hours, and nitroglycerin at a lower temperature, the trinitrobenzene derivatives require, in general, temperatures of 140° to 180° in order to give readily measurable volumes of gas on heating for 100 hours. The dinitro-compounds show scarcely any measurable decomposition. The nitroamines, such as tetryl, on the other hand, are less stable, and decompose sufficiently rapidly for measurements at 120°.

In order to give an approximate idea of the relative stability, the temperatures may be calculated by extrapolation, at which the gas evolution amounts to 1 c.c. per gram in 100 hours:

Trinitrobenzene	190—195°
Trinitrophenol	150—155°
2 : 4 : 6-Trinitrotoluene	135—140°
2 : 3 : 4- ,,	135—140°
3 : 4 : 6- ,,	130—135°
Trinitrophenylmethylnitroamine	115—120°
Cellulose nitrate (N = 13 per cent)	Approx. 100°

Trinitrotoluenes gave 0·8 to 1·8 c.c. of gas per gram in 100 hours at 140°. The differences in velocity between different samples indicated the presence of traces of catalysts, although most of the samples were very pure. There was practically no parallelism between the melting point and stability. The rate of evolution showed no acceleration; hence no autocatalysis occurred within limits measured. From the results obtained, it is evident that pure trinitrotoluene could be kept indefinitely at the ordinary temperature, but the actual rate of decomposition cannot be ascertained by direct extrapolation, as the results obtained in the case of tetryl have shown that a great increase in stability occurs on passing from the molten to the solid condition.

The isomeric trinitrotoluenes which accompany the symmetrical compound in small proportion on nitration of toluene were also

examined. The commercial products contained impurities which decreased their stability. When these were removed by crystallisation, 2:3:4-trinitrotoluene showed about the same stability as the 2:4:6-isomeride, whilst 3:4:6-trinitrotoluene was somewhat less stable. The stability of 2:4:6-trinitrotoluene was not sensibly affected by the addition of 1 per cent. of the other pure isomerides, but 5 per cent. of the 3:4:6-isomeride caused a slight increase of velocity.

Mixtures of picric acid and trinitrotoluene showed a lower rate of decomposition at 140° than trinitrotoluene alone. This was somewhat surprising, since the general experience is that acids decrease the stability. It is possible that the trinitrotoluene exists as an equilibrium in which a small quantity of an *iso*nitro-compound is present, the latter being the cause of the instability observed. Picric acid might readily cause the *iso*nitro-compound to revert to the normal nitro-compound, thus increasing the stability.

As an example of an unsaturated substance, castor oil was mixed with trinitrotoluene and with picric acid, and the mixtures were tested. The castor oil depressed the stability very strongly in both cases.

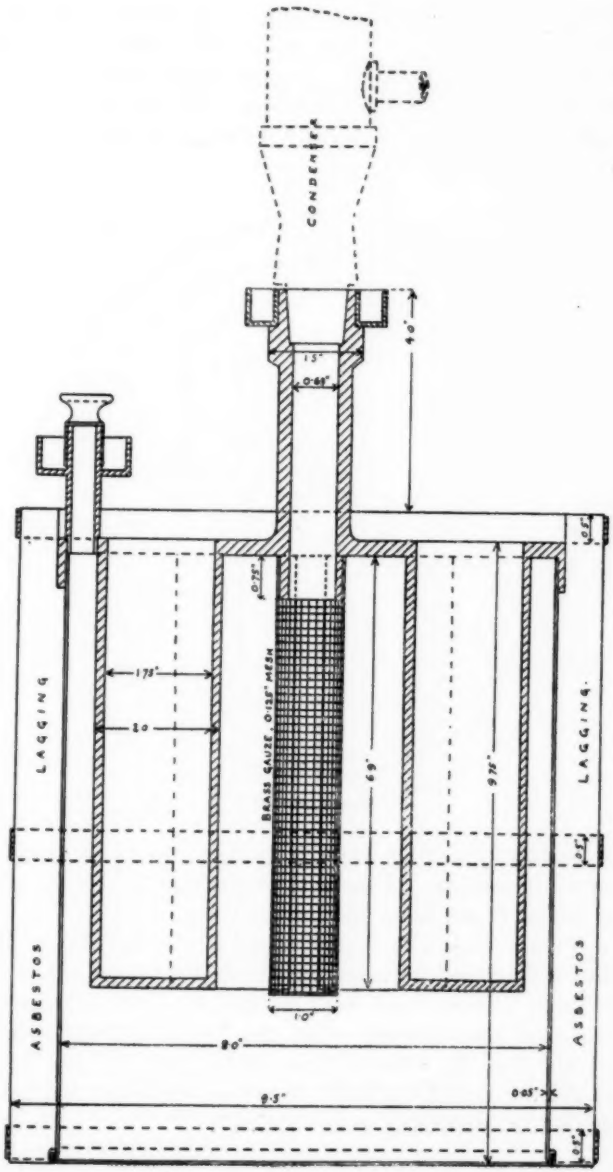
Trinitrophenol showed a stability intermediate between that of trinitrobenzene and that of trinitrotoluene. Trinitrobenzene showed extreme stability, even at the boiling point of aniline, and the stability was not perceptibly affected by wet and dry storage trials. This is of interest as showing that, notwithstanding the difficulty of introducing the third nitro-group, the trinitro-compound, when once prepared, is very stable.

Experimental.

Apparatus.—The thermostat (Fig. 1) consists of a cylindrical copper bath, which is maintained at the required temperature by a boiling liquid. The cover consists of a thin brass casting with six orifices for the heating tubes, and a short column to support the condenser. These all form part of the casting, thus avoiding joints, which are otherwise very apt to leak during protracted tests. The connexion with the condenser is made by a conical joint surmounted by a cap, which can be filled with vaselin or other material to lute the joint. The brass column also projects about 0·5 cm. into the interior of the bath, and is connected with a cylinder of coarse copper gauze of the same diameter as the tube and about 15 cm. in length. The object of this is to convey the condensed liquid down the centre of the bath and ensure uniform

heating. The lid has also a small opening for filling the bath. This is fitted with a cap and a cup for luting. A cylinder of lagging material surrounds the bath. The top of the bath is also

FIG. 1A.



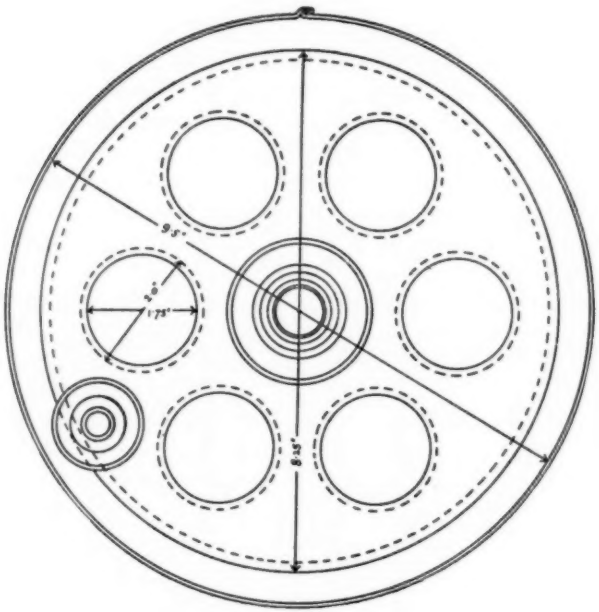
covered with a loose cake of asbestos lagging material about 3 cm. thick, with holes corresponding with those in the brass cover.

The condenser (Fig. 2) is of the multitubular pattern, and the water inlet tube is fitted with a funnel, as shown, so that the flow of water can be seen.

For temperatures from 80° to 100°, mixtures of alcohol and water were used. From 100° to about 135°, solutions of calcium chloride were generally taken. In the latter case, the addition of a little lime is advisable to avoid corrosion of the copper.

The temperature of the boiling calcium chloride solution is

FIG. 1B.

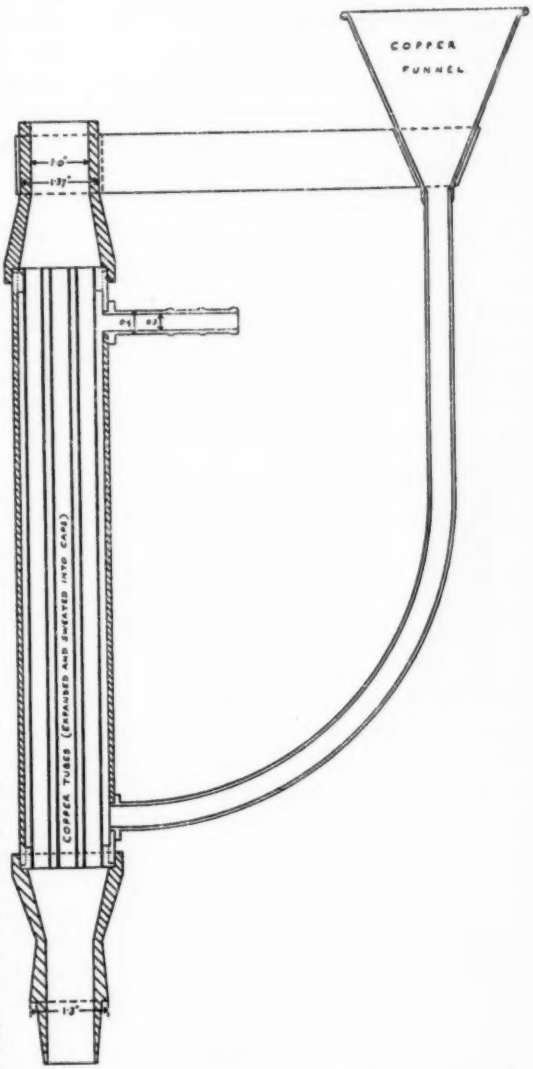


readily adjusted by adding water if too high, or by allowing water to evaporate if too low. The level of the liquid should be maintained at about 5 cm. from the lid of the bath.

Safety Precautions.—To guard against damage by explosion, steel tubes with closed bottoms were provided; these fitted loosely into the brass orifices, and were packed round with fine copper fillings to give good contact with the bath. They were made rather short (Fig. 3), since it was found that if they extended nearly to the surface of the bath, they became cooled by radiation, and irregular temperatures were obtained.

The thermostats were surrounded by screens and placed in a fire-proof shed. A cistern was provided to guard against failure of the water supply, and an automatic ball-cock tap was fitted to cut off the gas supply in case the cistern became empty.

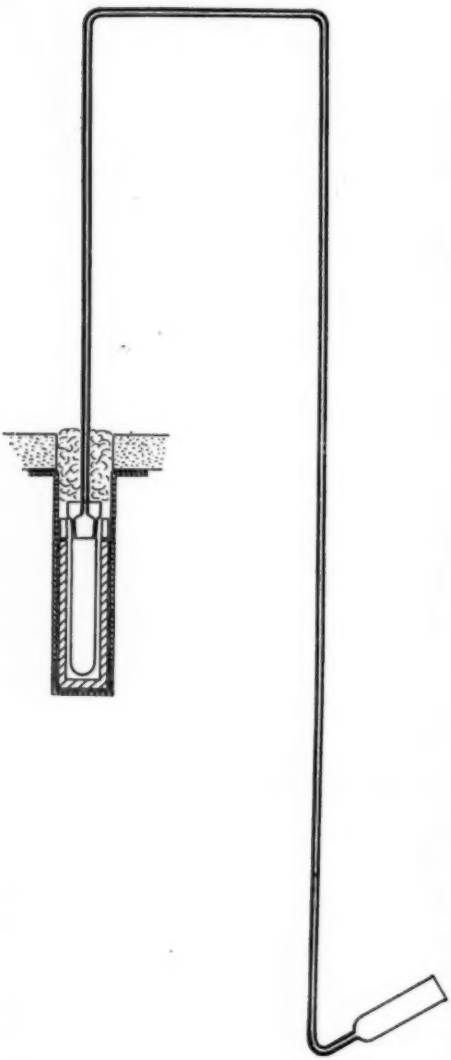
FIG. 2.



Heating Tubes. — The glass apparatus passed through numerous modifications in the course of a large number of measurements. The earlier patterns were fitted with glass taps for exhaustion, but it was found much better to avoid these, and the simple device shown in Fig. 3 was found to be a great improvement. In order to exhaust the tube, a quantity of mercury sufficient to fill the upright limb of the capillary tube is placed in the lower cup. This cup is connected with the pump by means of a rubber stopper. The apparatus is then inclined so that the cup is horizontal and the mercury lies in a pool in the cup, leaving a free passage between the pump and the capillary tube.

After exhaustion, the apparatus is returned to the upright position, and, on releasing the vacuum, the mercury rises in the capillary tube, which acts as a manometer during the test. The cup at the top of the heating tube is luted with mercury, and the apparatus is then ready to be transferred to the thermostat. It is important that the stopper be very well ground, and lubricated as thinly as possible with a non-reactive lubricant.

FIG. 3.



The thermometer is embedded in sand in a similar heating tube, which is introduced into one of the steel tubes and placed in the bath. Accuracy of the temperature readings is of great importance in view of the high temperature-coefficients of the decompositions.

Method of Working.—Very thorough cleaning of the apparatus is necessary, as traces of foreign matter have a marked catalytic effect. The tubes were cleaned successively with acetone, benzene, and hot chromic acid, and were then subjected to prolonged washing with water. The manometers were similarly cleansed. The complete removal of moisture is also of importance, since this frequently gives rise to abnormal accelerations. The explosive is dried at a temperature well below its decomposition point, and weighed quantities are introduced into the test-tubes. These are

then connected with the capillary tubes, the ground stoppers being thinly lubricated. The apparatus is then exhausted to about 5 mm. of mercury by means of a Geryk pump, and is heated to a temperature at which no measurable decomposition will occur (generally 80°) for some hours to remove water.

The apparatus is then again exhausted, dry air is allowed to enter through a three-way cock attached to the pump, and removed once more by the pump, and the apparatus is inserted in the thermostat. A little asbestos wool is packed round the stopper.

The time at which the heating commences is noted, and an arbitrary period is allowed to permit the pressure to settle down before the first reading is taken. This is necessary, on account of minute traces of residual volatile matter, and in some cases the volatility of the compound itself. In general, one and a-half hours have been found sufficient. The height of the mercury column is then read at intervals, in comparison with the barometric height. It is convenient to use, as barometer, a similar tube exhausted and placed near the apparatus. This automatically corrects the reading for temperature of the mercury and capillary depression.

To avoid differences in the level of the mercury in the lower cup, it is convenient to fill this up, so that it overflows into a dish as the mercury descends in the capillary tube.

In taking a number of readings, a sliding scale may be used with advantage. The zero is set to the mercury level in the barometer, and the difference between manometer and barometer can then be read off directly.

Calculation of Gas Volume.—The calibration of the apparatus includes measurements of the volume of the test-tube, the volume of unit length of the capillary, and the total length of the three limbs of the capillary tube from the stopper to a point on the capillary-tube level with the average height of mercury in the cup. The volume of explosive is deducted from the volume of the heating tube to obtain the net volume.

In calculating repeated readings with the same explosive and the same bath temperature, the following shortened method of calculation is useful: The bath temperature is practically constant; the ordinary temperature alters somewhat, but as this only affects the correction of the volume in the capillary tube, it may also be taken as constant (it was, in general, about 30°).

If the difference between barometer and manometer reading be p mm., the corrected volume of gas in the heating tube is equal to:

$$\text{Net gas space} \times \frac{273}{273 + \text{bath temp.}} \times \frac{p}{760}.$$

The corrected volume of gas in the capillary tube is equal to (total length $-760+p$) $\times$ (vol. of 1 mm.) $\times \frac{273}{303} \times \frac{p}{760} = p$ (total length -760) $\times$ (vol. of 1 mm.) $\times \frac{1}{843} + p^2$ (vol. of 1 mm.) $\times \frac{1}{843}$.

Hence the corrected volume is equal to

$$p\,(a+b)+p^2c,$$

where $a = \dfrac{\text{net gas space} \times 273}{760\,(273+\text{bath temp.})}$;

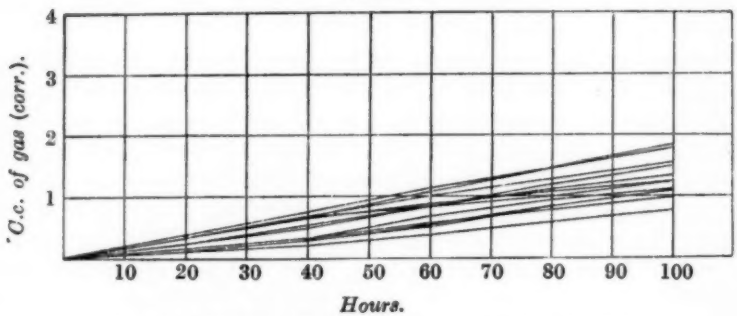
$b = \dfrac{1}{843}$ (length of capillary tube -760) $\times$ (vol. of 1 mm.)

$c = \dfrac{1}{843}$ (vol. of 1 mm.).

These constants can be determined for the whole series of measurements, and the calculation is then very simple. The constants b and c depend only on the calibration of the apparatus; a depends also on the volume of explosive and the bath temperature.

Correction for Fluctuations in Bath Temperature.—The fluctuations due to alteration of boiling point with variations of the barometric pressure are of importance, as the velocity of decomposition usually increases approximately 100 per cent. for each 5 degrees, or 15 per cent. per degree. It is better to apply the correction to the time readings rather than to correct the

FIG. 4.



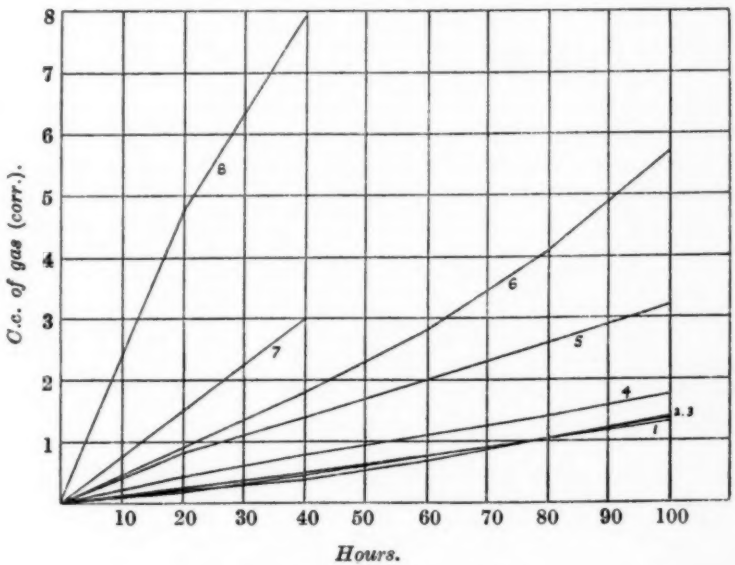
2 : 4 : 6-*Trinitrotoluene* (*various samples*) *at* 140°.

volume of gas from the individual tubes in the bath. If the deviation of temperature is within about 0·3°, it is generally sufficient to calculate a time correction for each day's readings, based on the mean temperature of the bath. Thus a deviation of 0·1° corresponds with a difference of 1·4 per cent. in the velocity, or 0·34 hour per day.

Measurements of Gas Evolution.

2:4:6-*Trinitrotoluene.*—Measurements at 120° gave very low results (about 0·15 c.c. in 100 hours). At 180° the evolution was too rapid and gave erratic accelerations, which made the measurements untrustworthy for comparison. Convenient velocities were obtained at 140°, and the following measurements were made on trinitrotoluenes from different sources (Fig. 4).

FIG. 5.



Trinitrotoluene isomerides at 140°.

Gas Evolution at 140° (*c.c. per gram*).

Melting point.	20 hours.	40 hours.	60 hours.	80 hours.	100 hours
81·1°	0·35	0·69	1·04	1·31	1·56
81·05	0·39	0·78	1·16	1·47	1·75
81·05	0·12	0·33	0·70	0·94	1·13
81·0	0·14	0·28	0·54	0·85	1·13
81·0	0·16	0·32	0·55	0·85	1·13
81·0	0·16	0·35	0·58	0·78	0·99
81·0	0·12	0·22	0·37	0·57	0·77
80·95	0·25	0·50	0·86	1·21	1·50
80·95	0·14	0·28	0·52	0·83	1·10
80·75	0·33	0·68	0·86	1·01	1·26
80·65	0·26	0·54	0·85	1·13	1·36
80·65	0·33	0·71	0·90	1·07	1·24
78·80	0·36	0·71	1·09	1·45	1·80

Comparative measurements on dinitrotoluene gave no perceptible decomposition in 100 hours.

2:3:4-*Trinitrotoluene*.—The following figures show the gas evolution after one and two crystallisations respectively. The purification reduced the rate of decomposition slightly.

Gas Evolution at 140° (*c.c. per gram*).

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.	
One crystallisation ...	0·44	0·78	1·07	1·40	1·75	Fig. 5 (4)
Two crystallisations ...	0·18	0·46	0·76	1·05	1·36	„ (3)
„ „ ...	0·22	0·37	0·67	1·01	1·38	„ (2)
2:4:6-T.N.T. (mean)	0·24	0·49	0·77	1·04	1·29	„ (1)

3:4:6-*Trinitrotoluene*.—The commercial product was much less stable than the above, and decomposed so rapidly at 140° that the measurement had to be made at 120°. The results after one crystallisation are given at both temperatures.

Gas Evolution at 120° (*c.c. per gram*).

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
Original (sample *a*)	2·2	3·3	—	—	—
One crystallisation	0·55	1·08	1·58	2·05	2·48

Gas Evolution at 140° (*c.c. per gram*).

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.	
Sample (*a*) One cryst.	4·7	7·9	—	—	—	Fig. 5 (8)
„ Two „	1·50	3·00	—	—	—	„ (7)
Sample (*b*) One cryst.	0·89	1·80	2·80	4·10	5·70	„ (6)
„ Two „	0·76	1·38	1·99	2·60	3·23	„ (5)

Even after purification, this isomeride was much less stable than 2:3:4-trinitrotoluene.

Mixtures of the Isomeric Trinitrotoluenes.—In order to ascertain whether the unsymmetrical isomerides, which always accompany 2:4:6-trinitrotoluene in small quantity in the crude product, affect the stability, the following mixtures were examined.

Gas Evolution at 140° (*c.c. per gram*).

2 : 3 : 4-T.N.T., per cent.	3 : 4 : 6-T.N.T., per cent.	Sample.	Purification.	2 : 4 : 6-T.N.T., per cent.	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
—	—	—	—	100	0·16	0·34	0·57	0·78	0·99
1	—	*a*	coml.	99	1·03	1·55	2·12	2·60	3·01
1	—	*b*	coml.	99	0·23	0·80	1·40	2·01	2·53
1	—	*b*	2 crysts.	99	0·15	0·33	0·55	0·79	0·98
5	—	*a*	coml.	95	2·23	3·34	4·21	4·99	5·78
5	—	*a*	1 cryst.	95	0·31	0·77	0·98	1·23	1·52
5	—	*b*	1 cryst.	95	0·54	0·87	1·10	1·36	1·69
5	—	*b*	2 crysts.	95	0·17	0·44	0·52	0·78	0·98
—	1	*b*	1 cryst.	99	0·48	1·11	1·61	2·10	2·53
—	1	*a*	2 crysts.	99	0·10	0·67	1·02	1·37	1·62
—	1	*b*	2 crysts.	99	—	—	—	—	1·28
—	5	*a*	2 crysts.	95	2·01	2·85	3·45	4·02	4·60
—	5	*a*	2 crysts.	95	1·56	2·51	3·22	3·85	4·44
—	5	*b*	2 crysts.	95	—	—	—	—	2·71

Influence of Picric Acid on the Stability of 2 : 4 : 6-*Trinitrotoluene*.—A trinitrotoluene was tested alone and in admixture with picric acid. The evolution from the mixture was less than from trinitrotoluene alone.

		C.c. of gas (corr.) (140°).						
Picric acid.	2 : 4 : 6-T.N.T.	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.	150 hours.	200 hours.
2	—	0·14	0·25	0·29	0·35	0·44	0·62	0·83
2	2	0·14	0·22	0·25	0·32	0·42	0·62	0·81
2	2	0·15	0·23	0·28	0·34	0·43	0·68	0·95
—	2	0·25	0·50	0·74	0·96	1·19	1·94	2·88

Influence of Unsaturated Compounds.—To avoid a disturbing effect on the gas volume due to vapour pressure, castor oil was chosen, as a fairly non-volatile, unsaturated substance. This increased the rate of decomposition very strongly; even at 120°, the gas evolution from trinitrotoluene containing 5 per cent. of castor oil was readily measurable.

		C.c. of gas (corr.) (120°).						
2 : 4 : 6-T.N.T.	Castor oil.	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.	150 hours.	200 hours.
5	0·25	0·65	1·00	1·90	2·80	3·75	7·60	11·10

Naphthalene under similar conditions gave no measurable gas evolution in admixture with trinitrotoluene, even when present to the extent of 40 per cent.

Picric Acid.—Measurements were made at 140° and 183° on picric acid crystallised from water. The gas evolution was very rapid at the higher temperature, but showed some decrease in velocity as the decomposition proceeded, from which it would

appear that some catalyst was being gradually eliminated. The successive crystallisations did not reduce the rate of decomposition at 183°, but at 140° some stabilisation was noticeable in the latter crystallisations.

Gas Evolution at 140° (*c.c. per gram*).

	100 hours.	150 hours.	200 hours.	300 hours.
Original	0·11	0·27	0·44	0·88
Cryst. No. 2	0·13	0·35	0·51	0·92
„ „ 4.....	0·04	0·12	0·23	0·50
„ „ 5.....	0·06	0·21	0·31	0·58

Gas Evolution at 183° (*c.c. per gram*).

	1 hour.	2 hours.	3 hours.	5 hours.	10 hours.	15 hours.	20 hours.
Cryst. No. 1	2·90	4·50	5·45	6·45	—	—	—
„ „ 2	2·95	4·85	6·10	7·30	—	—	—
„ „ 3	2·30	3·95	5·20	6·15	8·35	10·60	12·80
„ „ 4	1·90	3·80	5·50	6·65	9·00	11·35	13·65
„ „ 5	2·05	3·90	5·65	6·95	9·20	11·50	13·80

As in the case of trinitrotoluene, castor oil increased the decomposition. Whereas picric acid alone gave practically no measurable decomposition at 120°, a mixture of picric acid with 5 per cent. of castor oil gave the following evolution:

Picric Acid, 5 *grams. Castor Oil,* 0·25 *gram.*

	50 hours.	100 hours.	150 hours.	200 hours.
C.c at 120°.....	0·85	2·50	4·70	6·85

1:3:5-*Trinitrobenzene.*—The gas evolution from this compound was very low, even at 183° (boiling aniline bath). The following rates of decomposition were obtained with different samples:

Gas Evolution at 183° (*c.c. per gram*).

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
	0·05	0·14	0·20	0·27	0·33
	0·04	0·09	0·13	0·18	0·23
	0·03	0·07	0·10	0·14	0·19
	—	0·10	0·13	0·15	0·18
	—	0·10	0·13	0·15	0·18
	—	0·15	0·19	0·25	0·30
Mean.....	0·04	0·11	0·15	0·19	0·23

In order to ascertain the effect of storage on the stability, samples were kept for a year at 50°, and tested as above at 183°.

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
	0·07	0·13	0·18	0·24	0·30
	0·08	0·13	0·17	0·23	0·28
	0·06	0·10	0·17	0·22	0·27
	0·06	0·07	0·16	0·22	0·26
Mean.....	0·07	0·11	0·17	0·23	0·28

The influence of hydrolysis was examined by keeping samples for a year in a saturated atmosphere at 45° and testing at 183°.

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
	0·04	0·08	0·13	0·17	0·17
	0·02	0·04	0·12	0·25	0·24
	0·01	0·02	0·10	0·11	0·15
Mean.....	0·02	0·05	0·12	0·18	0·19

The effect of an admixture of picric acid on trinitrobenzene was tried at 150°, as the decomposition of picric acid itself is too rapid at 183°.

Gas Evolution at 150°.

	100 hours.	200 hours.	300 hours.	400 hours.	500 hours.
Picric acid, 0·2 gram Trinitrobenzene, 1·8 grams } ...	0·07	0·26	0·86	1·45	2·22
Trinitrobenzene 1·8 grams	0·07	0·07	0·20	0·28	0·60

Summary.

An apparatus is described for the determination of stability of high explosives by the velocity of evolution of gas on heating in a vacuum.

All explosives appear to be liable to a gradual decomposition at temperatures considerably below their ignition points. The velocity is highly affected by temperature and by the catalytic action of impurities.

Trinitrotoluene and the isomerides which accompany it on nitration of toluene do not differ greatly in stability when purified. Trinitrobenzene is much more stable, notwithstanding the difficulty with which it is prepared by nitration, and trinitrophenol shows an intermediate stability.

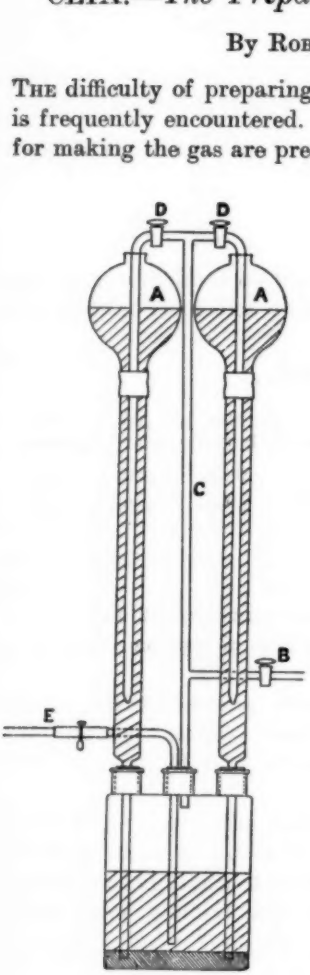
The thanks of the author are due to the Director of Artillery for permission to publish these results.

Research Department,
Royal Arsenal, Woolwich. [*Received, November 3rd,* 1920.]

CLIX.—*The Preparation of Pure Carbon Dioxide.*

By Robert Crosbie Farmer.

The difficulty of preparing carbon dioxide completely free from air is frequently encountered. Notwithstanding that all solutions used for making the gas are previously boiled, the elimination of the last traces of air is very difficult, and the same applies to carbon dioxide from cylinders, even though most of the gas is blown to waste beforehand, to eliminate the air as far as possible. The difficulty is especially noticeable in the testing of the stability of gun-cotton by Will's method (*Zeitsch. angew. Chem.*, 1901, **14**, 743, 774), in which a relatively large quantity of carbon dioxide is used to sweep out the nitrogenous gases, and the air-correction forms a very high proportion of the unabsorbed gases.



By the following simple method, which has been used very satisfactorily for some time in connexion with the Will test, the proportion of air in carbon dioxide can be reduced to such a degree that it is practically immeasurable. The method depends upon the principle that a dissolved gas can be very completely removed from a liquid by bubbling a second gas through the liquid. The carbon dioxide is prepared from solutions of potassium hydrogen carbonate and sulphuric acid, each of which is freed from air by bubbling carbon dioxide through it, before the two are brought together.

The generator is shown in the figure. The pear-shaped funnels, *A A*, contain potassium hydrogen carbonate (300 grams to 1 litre of water) and sulphuric acid (120 c.c. to 1 litre of water) respectively. The solutions should be previously filtered through glass-wool. From the funnels these solutions pass down the broad verti-

cal tubes into the generating bottle. The bulk of the carbon dioxide is drawn off at *B* and used as required. A small proportion of the gas is, however, allowed to pass through the tube *C*, and bubbles through the columns of liquid in the two upright tubes, thus removing all traces of dissolved air. If desired, a separate source of carbon dioxide can be used for this purpose. As soon as the air originally present in the Woulfe's bottle has been eliminated, the carbon dioxide reaches a state of extreme purity, and gives practically no residue of gas on absorption with potassium hydroxide solution.

The fittings of the Woulfe's bottle must be absolutely free from leaks; the bottle may, if desired, be immersed in water covered with a layer of paraffin wax. The feed tubes dip below the surface of mercury to avoid back-diffusion. If the whole apparatus is mounted on a stand, it can be tilted slightly to equalise the back pressure in the two feed tubes, but no very accurate balancing is necessary. A little methyl-orange in the solution serves to show that the solutions are being mixed in about the right proportions.

Once started, the apparatus need never be disconnected. When the tap *B* is turned off, the introduction of the reagents automatically ceases. The taps *DD*, which regulate the bubbles of gas, should, however, be closed when the apparatus is not in use. The spent liquor can be drawn off at *E*, as the fresh solutions are added. The rate of evolution can be increased almost indefinitely by using a somewhat larger apparatus.

The thanks of the author are due to the Director of Artillery for permission to publish this note.

RESEARCH DEPARTMENT,
ROYAL ARSENAL, WOOLWICH. [*Received, November 3rd,* 1920.]

CLX.—*Triphenylarsine and Diphenylarsenious Salts.*

By WILLIAM JACKSON POPE and EUSTACE EBENEZER TURNER.

THE introduction of aromatic arsenic compounds as materials for chemical warfare rendered necessary the working out of satisfactory methods for preparing triphenylarsine, $(C_6H_5)_3As$, and diphenylchloroarsine, $(C_6H_5)_2AsCl$. The former of these two compounds is conveniently prepared by Michaelis and Reese's method (*Ber.*, 1882, **15**, 2876), which consists in treating an ethereal solution of arsenic trichloride and bromobenzene with sodium; in

a later paper (*Ber.*, 1886, **19**, 1031), Philips showed that chlorobenzene can be substituted for bromobenzene, and that the reaction is stimulated by the addition of a small proportion of ethyl acetate, but, more recently (*Annalen*, 1902, **321**, 160), Michaelis claimed that a cleaner product is obtained by the use of bromobenzene than of chlorobenzene.

The several workers on this reaction used ether as a solvent, and it was important to ascertain whether this could be replaced by some less volatile and less inflammable diluent. Preliminary experiments showed that the reaction proceeds better in benzene than in ethereal solution, and that, contrary to Michaelis's suggestion, chlorobenzene gives a cleaner product than does bromobenzene. It was thus shown that triphenylarsine is readily prepared by the action of sodium on a mixture of arsenic trichloride and chlorobenzene in benzene solution to which a little ethyl acetate had been added; this method was described in a report to the Chemical Warfare Department, dated January 28th, 1918, and formed the basis of the larger-scale work done by Morgan and others (this vol., p. 777) in the conversion of the laboratory method into a works process.

It was observed that the use of ether as a diluent is disadvantageous, in that the violent reaction tends to pass out of control, and that, when this happens, pyrophoric sodium remains after the evaporation of the ether, causing dangerous fires. The repetition of the method of Philips gave a yield of 71 per cent. of the theoretical; Michaelis's later method gave a yield of 67 per cent. of the theoretical. In the absence of a diluent, sodium acts on a mixture of arsenic trichloride and chlorobenzene causing incandescence.

Experiments were next carried out for the purpose of ascertaining how the yield of triphenylarsine is influenced by the proportions of the reacting materials and by the conditions. The general method adopted was to weigh out the sodium in slices (*s*), granules (*g*), powder (*p*), or wire into a large flask, cover with benzene containing 1 or 2 per cent. of ethyl acetate, allow to remain for half an hour to activate the metal, and then slowly run in the arsenic trichloride and chlorobenzene. After a few minutes, a vigorous reaction sets in, which, when sodium wire is used, must be controlled by the use of a freezing mixture; when sliced sodium is used, no external cooling is necessary, and, indeed, once the reaction is checked by cooling, it can only be started again with considerable difficulty. The mixture is then left overnight, filtered, and the inorganic residue well washed with hot benzene; the filtrate and washing are distilled until a thermometer placed

in the liquid registers 200°. The residue solidifies on cooling to a crystalline mass, and is almost pure triphenylarsine; in general, it melts at above 56°.

The following table gives the results of a series of experiments, in each of which 136 grams of chlorobenzene were used; this quantity requires theoretically 60 grams of arsenic trichloride and 46 grams of sodium for complete conversion into triphenylarsine.

No. of experiment.	Volume of benzene. C.c.	Sodium. Grams.	Form of sodium.	$AsCl_3$. Grams.	Percentage of theoretical yield of C_6H_5Cl used.
1	400	68	s	72	67·5
2	,,	,,	,,	,,	69
3	,,	,,	,,	,,	66
4	,,	,,	,,	,,	64
5	,,	,,	,,	,,	62·5
6	,,	,,	,,	,,	71
7	,,	,,	p	,,	83
8	,,	,,	s	80	91·5
9	,,	,,	,,	85	95·5
10	,,	,,	,,	90	93·5
11	,,	63	,,	80	80
12	,,	60	g	,,	75
13	350	,,	s	,,	83·5
14	,,	56	,,	90	81
15	300	60	,,	85	88
16	,,	57	,,	,,	93
17	,,	,,	,,	90	89
18	,,	,,	g	85	80
19	,,	55·5	s	90	83
20	,,	,,	,,	95	74·5
21	,,	,,	,,	90	84

Experiments 1 to 3 were carried out just as described above; 4 and 5 were carried out as rapidly as possible, and the product was worked up immediately without remaining overnight. In numbers 6 and 7 the product was gently boiled under reflux for several hours after the spontaneous reaction had ended. It is thus shown that the yield is not improved by hastening the reaction, but that it does increase when the reaction is continued further by boiling; the operation of boiling under reflux was therefore introduced in all the later experiments. A consideration of the further experiments shows that the yield of triphenylarsine, calculated on the amount of chlorobenzene used, is appreciably raised by increasing the amount of arsenic trichloride to 85 grams, and is practically unaffected by diminishing the weight of sodium to 57 grams; it appears, further, that the volume of benzene used can be reduced to 300 c.c. without ill-effect on the yield. The most satisfactory results seem to be obtained by using 300 c.c. of benzene for each 136 grams of chlorobenzene, 85 grams of arsenic trichloride, and 57 grams of sodium, but since the

reaction proceeds well with considerable fluctuations of the proportions, the appropriate quantities of materials to be used depend on the relative cost of the latter.

The reaction between chlorobenzene and arsenic trichloride is not promoted by boiling with copper or aluminium powder, the copper–zinc couple, or magnesium or calcium turnings. The copper arsenide obtained by digesting a hydrochloric acid solution of arsenic trichloride, collecting the black powder, washing it with water and acetone, and drying, is without action on chlorobenzene, but when heated with iodobenzene yields diphenyl.

Conversion of Triphenylarsine into Di- and Mono-phenylarsine Derivatives.

Michaelis and Reese showed (*Ber.*, 1882, **15**, 2876) that phenylarsenious dichloride is produced on heating triphenylarsine with arsenic trichloride under pressure; it is to be concluded that diphenylarsenious chloride is formed as an intermediate stage, and particulars have been given by Morgan and Vining (this vol., p. 780) of a convenient means for preparing diphenylarsenious chloride by heating triphenylarsine with arsenic trichloride at 250—280° under pressure. This method involves, however, the use of an autoclave, and it seemed of interest to ascertain whether the same reaction could be carried out under the ordinary atmospheric pressure.

Triphenylarsine (30·6 grams) was maintained at 350° while arsenic trichloride (25·5 c.c.) was very slowly run in by means of a long capillary tube; the arsenic trichloride which distilled over was returned to the reaction vessel. The first addition of the arsenic trichloride occupied one and three-quarter hours. On carefully distilling the product under 12—15 mm. pressure, the following fractions were obtained at above 120°: (*a*) 120—160°, 17·7 grams; (*b*) 160—200°, 22·2 grams; (*c*) 200—250°, 2·2 grams; (*d*) residue, 2·2 grams. The fraction (*a*) is fairly pure phenylarsenious dichloride, (*b*) is pure diphenylarsenious chloride, whilst (*c*) and (*d*) consist of nearly pure triphenylarsine; allowing for the recovery of the latter, the yield of phenylarsenious dichloride and diphenylarsenious chloride is 97 per cent. of the theoretical.

In the experiment just described, the arsenic trichloride was added fairly rapidly, and another may be quoted to show the effect of running it in more slowly. Using the same quantities as before, but taking seven hours for the addition of the arsenic trichloride, the following fractions were obtained on distilling the product under 12—15 mm. pressure: (*a*) 120—160°, 12 grams of

moderately pure phenylarsenious dichloride; (*b*) 160—205°, 31·5 grams of practically pure diphenylarsenious chloride; and a residue (*c*) of 7·2 grams of impure triphenylarsine. In this case, a larger proportion of diphenylarsenious chloride was produced.

The general conclusion is drawn from the above and other experiments that, under atmospheric pressure, the following reactions occur: $(C_6H_5)_3As + 2AsCl_3 = 3(C_6H_5)AsCl_2$ and

$$2(C_6H_5)_3As + AsCl_3 = 3(C_6H_5)_2AsCl.$$

In addition to the foregoing, the reaction represented by the following equation may also occur:

$$(C_6H_5)AsCl_2 + (C_6H_5)_3As = 2(C_6H_5)_2AsCl,$$

and experiment showed this reaction to take place almost quantitatively. On heating a mixture of triphenylarsine (15·3 grams) and phenylarsenious dichloride (11·2 grams) for four hours at 300° in an open flask, and distilling the resulting pasty mass under diminished pressure, nearly pure diphenylarsenious chloride (20 grams) distilled at 185°/15 mm.; this corresponds with a yield of about 80 per cent. of the theoretical; under the conditions stated, a small amount of chlorobenzene was produced, and practically no action occurs at 250°.

It is thus proved that the reaction between arsenic trichloride and triphenylarsine proceeds very satisfactorily under atmospheric pressure, and that the product is an equilibrium mixture resulting from the simultaneous occurrence of several reactions. In view of the possible importance of the observation that triphenylarsine can be converted into phenylarsenious dichloride and diphenylarsenious chloride by the action of arsenic trichloride under the ordinary pressure, the above and analogous reactions were protected by secret Patent No. 142880 of June 11th, 1918, of which the specification has now been published.

Diphenylarsenious Bromide, $(C_6H_5)_2AsBr$.

Diphenylarsenious oxide, $[(C_6H_5)_2As]_2O$, was prepared by Michaelis and La Coste (*Annalen*, 1880, **201**, 229), but the following is a more expeditious method for obtaining it in a pure state. Potassium hydroxide (12 grams) dissolved in water (10 c.c.) is added to rectified spirit (200 c.c.); a solution of diphenylarsenious chloride (53 grams) in spirit (100 c.c.) is added, and the mixture boiled for an hour. The solvents are then distilled off and the solid residue is extracted with chloroform; on drying, filtering, and evaporating the extract, a quantitative yield of pure diphenylarsenious oxide remains as a colourless, crystalline solid melting at 89—91°.

On heating the oxide at 100° with hydrobromic acid in a sealed tube and allowing to cool, diphenylarsenious bromide, $(C_6H_5)_2AsBr$, separates as a colourless, crystalline solid melting at 55—56°; this compound is described by Michaelis and La Coste as a yellow, oily liquid. The bromide is also obtained by heating triphenylarsine (30·6 grams) with arsenic tribromide (15·8 grams) for three hours at 300—350°; on distilling the product under 14 mm. pressure, the following fractions resulted: below 170°, 2 grams of a mixture of benzene and bromobenzene; 170—205°, 26 grams of crude diphenylarsenious bromide and a residue of 15 grams of mixed diphenylarsenious bromide and triphenylarsine. By redistillation, pure diphenylarsenious bromide was readily obtained.

Diphenylarsenious Iodide (*Diphenyliodoarsine*), $(C_6H_5)_2AsI$.

This previously undescribed substance is obtained by heating diphenylarsenious oxide (25 grams) with fuming hydriodic acid (30 grams) for two hours in a sealed tube at 100°; on cooling, the crude iodide (29·5 grams) solidifies and melts at 42—45°. On crystallisation from benzene, the compound is obtained in yellow, crystalline scales melting at 45—46° (Found: I = 35·6. $C_{12}H_{10}IAs$ requires I = 35·6 per cent.).

On heating triphenylarsine (30·6 grams) with arsenic tri-iodide (22·8 grams) for six hours in an open flask at 350—360° and distilling the resulting mass under diminished pressure, practically pure diphenylarsenious iodide (25 grams) distils at 204—218°/10 mm.; the yield is less than 50 per cent. of the theoretical, and the reaction does not proceed so satisfactorily as in the case of the corresponding bromo-derivative.

The work described in the present paper was carried out for the purposes of the Chemical Warfare Department, and permission for its publication has been given by the General Staff.

THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE. [*Received, October 15th,* 1920.]

CLXI.—*Interaction of Ethylene and Selenium Monochloride.*

By Harold William Bausor, Charles Stanley Gibson, and William Jackson Pope.

In a previous paper (this vol., p. 271) we have shown that ethylene is absorbed by sulphur monochloride, giving a quantitative yield of $\beta\beta'$-dichloroethyl sulphide, in accordance with the following equation:

$$2CH_2{:}CH_2 + S_2Cl_2 = (CH_2Cl{\cdot}CH_2)_2S + S.$$

It is now shown that ethylene reacts with selenium monochloride to give *$\beta\beta'$-dichloroethyl selenide dichloride* and selenium; the reaction proceeds in good accord with the following equation:

$$2CH_2{:}CH_2 + 2Se_2Cl_2 = (CH_2Cl{\cdot}CH_2)_2SeCl_2 + 3Se.$$

Whilst it thus appears that sulphur monochloride and selenium monochloride are acted on quite differently by ethylene, it is possible that the action proceeds analogously in both cases so as to yield $\beta\beta'$-dichloroethyl sulphide or selenide, but that the selenide is further acted on by selenium monochloride, giving selenium and the new derivative of quadrivalent selenium now described; this suggestion is supported by the observations of Evans and Ramsay (T., 1884, **45**, 64), which indicate that selenium monochloride readily decomposes into selenium and chlorine.

Preparation of Selenium Monochloride.

Selenium monochloride is conveniently prepared in quantity by a modification of the method described by Divers and Shimose (T., 1884, **45**, 198). Finely powdered selenium (80 grams) is added, with constant shaking, to fuming sulphuric acid (320 c.c.) containing 15 per cent. of dissolved sulphur trioxide; the mixture is warmed to 45—50°, with shaking, allowed to cool, and treated with a current of dry hydrogen chloride. When the gas is no longer absorbed, the product is poured into concentrated sulphuric acid (450 c.c.), and the residue washed in with the same liquid (25 c.c.); the lower layer of crude selenium monochloride containing suspended selenium, is drawn off, mixed with fuming sulphuric acid (containing 15 per cent. of sulphur trioxide) (100 c.c.), and treated with a brisk stream of dry hydrogen chloride for an hour and a-half. The product is now poured into concentrated sulphuric acid (150 c.c.), when much hydrogen chloride is evolved.

and the lower layer of selenium monochloride (99 grams) drawn off. Thus obtained, it forms a deep red liquid containing a little free selenium in suspension; it is further purified by keeping over dry potassium chloride and filtering in a dry atmosphere.

ββ′-Dichloroethyl Selenide Dichloride, $(CH_2Cl{\cdot}CH_2)_2SeCl_2$.

Selenium monochloride (55·5 grams) is dissolved in dry benzene (50 c.c.), and a current of dry ethylene passed through the solution; considerable evolution of heat occurs, and the liquid should be kept cool. Absorption commences rapidly, and selenium is almost immediately precipitated; it is desirable to add further quantities of dry benzene (20 c.c.) to prevent blockage of the delivery tube. When no further absorption occurs, more benzene is added, and the liquid filtered boiling hot, the residue being extracted with boiling benzene until the filtrate deposits no more crystalline product on evaporation. ββ′-Dichloroethyl selenide dichloride (27·5 grams) remains in the form of white, crystalline needles after distilling off the benzene, and may be purified from slight admixture with selenium by recrystallisation from boiling benzene. From observation of the quantity of selenium recovered (30·0 grams), it is concluded that the reaction proceeds in accordance with the equation given above.

ββ′-Dichloroethyl selenide dichloride is about ten times as soluble in boiling benzene as in the cold solvent; it crystallises in long, colourless prisms (see figure), which melt at 122·5°, and are slightly hygroscopic. The crystallographic description given below was furnished by Miss I. E. Knaggs, working under the direction of Mr. A. Hutchinson.

Crystal System.—Monosymmetric, holohedral.

Axial Ratios.—$a:b:c=0{\cdot}6345:1:0{\cdot}8389$. $\beta=75°50'$.

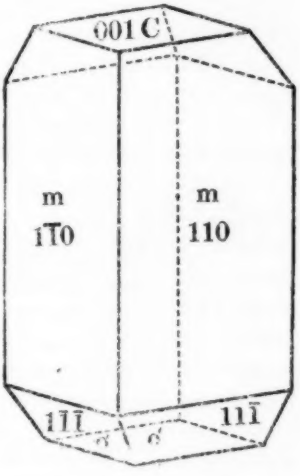
Forms Observed.—$C(001)$, $m(110)$, $o'(111)$.

Angle.	No. of measurements.	Limits.	Observed.	Calculated.
$mm=1\bar{1}0:\bar{1}10$	9	62°38′— 63°46′	63°12′	—
$mm=110:\bar{1}10$	9	116 14 —117 22	116 52	116°48′
$mo'=\bar{1}10:\bar{1}11$	9	35 25 — 36 24	36 2·5	—
$o'C=\bar{1}11:001$	7	65 24 — 66 43	66 2	65 59·5
$mC=\bar{1}10:001$	6	101 40 —102 23	102 2	—
$Cm=001:\bar{1}10$	7	77 25 — 78 28	77 49	77 58

No cleavage was observed. The crystal habit is prismatic, and is terminated by small basal and pyramidal planes. The crystal faces are very much rounded and badly developed, and it was only possible to obtain approximate angular measurements. The optic

axial plane is perpendicular to the plane of symmetry, and the acute bisectrix lies in the plane of symmetry, being inclined at 22° to the z-axis in the acute axial angle. The refractive index, β, was found by the immersion method to be approximately 1·65; the index, α, is slightly less than this, and γ is somewhat higher than 1·75, and could not be determined. The double refraction is hence strong and positive in sign; this was verified by observation on a section cut nearly perpendicular to the acute bisectrix. The optical axial angle was measured as 31°13′ for sodium light in a liquid of refractive index 1·65. Moderate dispersion of the optic axes was observed, the angle for red being greater than that for blue light; horizontal dispersion was not observed.

The compound dissolves freely in cold water to an acid liquid,



which gives a precipitate of silver chloride with the nitrate; a viscous liquid remains on evaporating the aqueous solution. One half of the chlorine present is hydrolysed to hydrogen chloride by the action of water (Found: C = 17·5; H = 2·70; Cl = 51·4; Se = 29·1. 0·1591 required 11·5 c.c. N/10-$AgNO_3$. Hydrolysable chlorine = 25·7. $C_4H_8Cl_4Se$ requires C = 17·3; H = 2·89; Cl = 51·3 per cent.).

On passing sulphur dioxide into a cold dilute aqueous solution of the dichloride, a heavy oil separates; this, when collected and left in a cool place, crystallises to a mass of almost colourless, prismatic needles. This compound is very readily soluble in benzene, and, when crystallised from a small quantity of this solvent, melts at 23—25°; it is possibly $\beta\beta'$-dichloroethyl selenide,

and, as special precautions must be observed in handling such a substance, its further examination will be continued later. We are engaged on the further study of the interaction of ethylene and other non-metallic chlorides.

The work described in the present paper was carried out for the purposes of the Chemical Warfare Department, and permission for its publication has been given by the General Staff.

THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE. [*Received, October 15th*, 1920.]

CLXII.—*Researches on Residual Affinity and Co-ordination. Part II. Acetylacetones of Selenium and Tellurium.*

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

THE acetylacetone derivatives of the metals, metalloids, and non-metals may be classified into three main groups.

I. Metallic acetylacetones, in which the principal valencies of the metal are completely satisfied by the univalent acetylacetone radicle, $C_5H_7O_2$, such as the thallous, glucinum, cupric, zinc, scandium, aluminium, chromic, ferric, and thorium derivatives, and numerous others. In many instances acetylacetone has given wings to the metals, for certain of these compounds are volatile without decomposition (Combes, *Compt. rend.*, 1894, **117**, 1222; Kurovski, *Ber.*, 1910, **63**, 1078; T., 1913, **103**, 81; 1914, **105**, 189).

II. Acetylacetones of the non-metals and metalloids, in which the principal valencies of the element are only partly satisfied by the univalent acetylacetone radicle. Such are the compounds of boron, silicon, and titanium, $B(C_5H_7O_2)_2Cl$, $Si(C_5H_7O_2)_3Cl$, and $Ti(C_5H_7O_2)_3Cl$, which function as metallic chlorides giving rise to remarkable double salts (Dilthey, *Annalen*, 1905, **344**, 326).

III. Acetylacetones of sulphur, which behave as true organic derivatives of sulphur, carbon being attached directly to this non-metal and not through the intermediary of oxygen, as in the two preceding classes (Angeli and Magnani, *Gazzetta*, 1893, **23**, ii, 415; 1894, **24**, i, 342; Vaillant, *Compt. rend.*, 1894, **119**, 647).

There is also a transition group of metallic acetylacetones between the main groups I and II, in which the principal valencies of the metal are only partly satisfied by the acetylacetone complex. This

transition group includes the complex acetylacetones of platinum (Werner, *Ber.*, 1901, **34**, 2584) and the cobaltic acetylacetone compounds of the general type $[C_5H_7O_2Co\ en_2]X_2$ (Werner, *Helv. Chim. Acta*, 1918, **1**, 78), where en = ethylenediamine. The latter series of acetylacetone derivatives exhibits optical activity and the existence of enantiomorphous pairs of isomerides affords definite information as to the arrangement of the acetylacetone nucleus in these substances, and justifies the belief that the univalent group $CH_3{\cdot}CO{\cdot}CH{:}C(CH_3){\cdot}O{\cdot}$ functions as two associating units,* forming a ring structure in which the metallic atom is implicated.

The research described below, which is still in a preliminary stage, shows that the interactions of acetylacetone and the tetrachlorides of selenium and tellurium lead to products differing considerably in type from those classified above. Although there are many points of difference between the various members of the three main groups of acetylacetone derivatives, they possess one attribute in common, namely, the univalent acetylacetone radicle, of which one or more are present in the molecule of every one of these derivatives hitherto described. In the acetylacetones of selenium and tellurium these metalloids are found to be associated with a bivalent radicle, $C_5H_6O_2''$.

Selenium tetrachloride and acetylacetone interact in ethereal solution in accordance with the following equation:

$$(1)\quad 2SeCl_4 + 4C_5H_8O_2 = [C_5H_6O_2{\cdot}{:}Se]_2 + 2C_5H_7ClO_2 + 6HCl,$$

the products being *selenium acetylacetone*, a well-defined, pale yellow, crystalline compound, chloroacetylacetone, and hydrogen chloride. This selenium acetylacetone, which is bimolecular in benzene solution, is readily decomposed by concentrated hydrochloric acid and by reducing agents, such as the alkali hydrogen sulphites. The former of these decompositions takes place readily, giving rise to elemental selenium and chloroacetylacetone,

$$(2)\quad [C_5H_6O_2{\cdot}{:}Se]_2 + 2HCl = 2Se + 2C_5H_7O_2Cl.$$

* The adjective "chelate," derived from the great claw or "chela" ("chely") of the lobster and other crustaceans, is suggested for these caliper-like groups which function as two associating units and fasten on to the central metallic atom so as to produce heterocyclic rings. Among the compounds which, by virtue of their residual affinity, function as chelate groups are ethylenediamine (en), propylenediamine, αα-dipyridyl and dimethylethylene sulphide (T., 1912, **101**, 1798). Many unsaturated radicles also function as chelate groups, partly owing to their principal valencies and partly owing to residual affinity, for example, the acetylacetone and oxalate groups, and the univalent groups in dimethylglyoxime,

$$CH_3{\cdot}C(:NOH){\cdot}C(CH_3){:}NO{\cdot},$$

nitroso-β-naphthol, $O{:}C_{10}H_6{:}NO{\cdot}$, and many other lake-forming complexes. In the present communication the bivalent radicle, $C_5H_6O_2''$, functions as a chelate group entirely owing to its principal valencies.

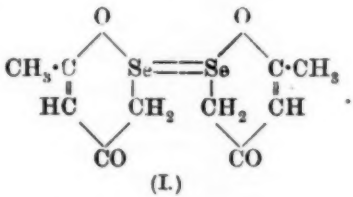
The latter decomposition, which proceeds quantitatively, is an interesting example of the way in which organic research sometimes leads to improvements in inorganic syntheses. Four molecular proportions of alkali hydrogen sulphite reduce the dimeric selenium acetylacetone quantitatively into acetylacetone and alkali selenodithionate:

$$(3)\ [C_5H_6O_2{:}Se]_2 + 4KHSO_3 = 2C_5H_8O_2 + 2Se{<}\begin{matrix}SO_3K\\SO_3K\end{matrix}.$$

In the earlier preparations these selenodithionates were obtained in a laborious manner, together with alkali thioselenates, by digesting sulphites with selenium or selenious acid (Rathke, *J. pr. Chem.*, 1865, **95**, 8; 1866, **97**, 56; Schultze, *ibid.*, 1885, [ii], **32**, 399).

The acetylacetone set free in the foregoing reduction and in other similar reactions is conveniently estimated by coupling with sodium *iso-p*-nitrobenzenediazo-oxide to form the sparingly soluble *p*-nitrobenzeneazoacetylacetone, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_5H_7O_2$ (Bülow and Schlotterbeck, *Ber.*, 1902, **35**, 2191).

The foregoing equations representing the formation and quantitative decompositions of selenium acetylacetone are consistent with the view that this associated compound may be represented by the graphic formula



(I.)

This conclusion is confirmed by the results obtained in studying the interaction of tellurium tetrachloride and acetylacetone. In moderately concentrated chloroform solution these reagents give rise to a colourless substance, *tellurium acetylacetone dichloride*,

$$(4)\ TeCl_4 + C_5H_8O_2 = C_5H_6O_2{:}TeCl_2 + 2HCl.$$

The dichloride when cautiously reduced with sulphurous acid or alkali hydrogen sulphites loses its chlorine and yields *tellurium acetylacetone*, a golden-yellow compound, which, unlike its selenium analogue, does not exhibit association in organic solvents:

$$(5)\ C_5H_6O_2{:}TeCl_2 + H_2SO_3 + H_2O = C_5H_6O_2{:}Te + 2HCl + H_2SO_4.$$

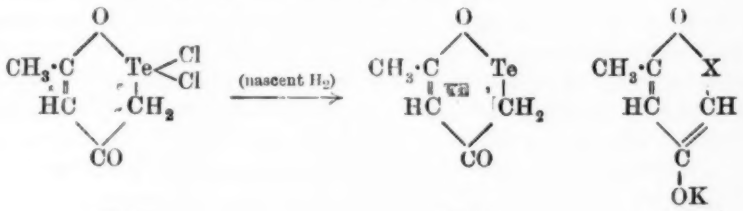
Tellurium acetylacetone is decomposed quantitatively into tellurium and acetylacetone by such reducing agents as an aluminium–mercury couple or alkali hydrogen sulphites. In the latter case a tellurium analogue of the alkali selenodithionates was not detected:

$$(6)\ C_5H_6O_2{:}Te + 2KHSO_3 = C_5H_8O_2 + Te + K_2SO_4 + SO_2.$$

Tellurium acetylacetone differs from the selenium analogue in its decomposition with cold concentrated hydrochloric acid (compare equation 2); it yields acetylacetone and half the tellurium as the tetrachloride:

$$(7)\quad 2C_5H_6O_2{:}Te + 4HCl = 2C_5H_8O_2 + Te + TeCl_4.$$

These reactions support the view that tellurium acetylacetone dichloride (II) and tellurium acetylacetone (III) may be represented respectively by the following formulæ:



(II.) (III.) (IV.)

Selenium and tellurium acetylacetones function as weak acids and dissolve in aqueous alkali hydroxides. It is therefore evident that they may have an alternative enolic configuration (IV), which would correspond with that of their unstable alkali salts.

Experimental.*

Selenium Acetylacetone, $[C_5H_6O_2{:}Se]_2$.

Selenium tetrachloride was prepared by passing dry chlorine in excess over coarsely powdered selenium at the ordinary temperature, the dark red monochloride being formed as an intermediate phase. The pale yellow, crystalline tetrachloride (14·3 grams) suspended in 140 c.c. of dry ether was treated at the ordinary temperature with 13 grams of acetylacetone (2 mols.) dissolved in 30 c.c. of the same solvent. Hydrogen chloride was forthwith evolved, the solution reddened, the tetrachloride slowly passed into solution, while a yellow precipitate appeared and redissolved in about thirty minutes to a transparent, pale red, fuming lachrymatory solution, which was evaporated rapidly at the ordinary temperature in a current of air. Hydrogen chloride, ether, and chloroacetylacetone were thus removed; the residue, a pale red oil, solidified on stirring. The product (10 grams, yield 90 per cent.) crystallised from benzene in pale primrose-yellow, glistening plates or lath-like needles, giving yellow solutions in organic media; on exposure to light for prolonged periods its surface became thinly coated with pink selenium.

* The authors are indebted to Dr. Scott for a gift of pure tellurium, and to Professor Ling for specimens of this metalloid and of selenium.

During this incipient decomposition the odour which at first was pleasing and farinaceous became faintly nauseating, a result which was due probably to liberation of traces of hydrogen selenide. The substance reddened at about 140°, and subsequently melted and decomposed at 175°. In a sealed capillary tube heated from 150° it melted to an orange-red liquid at 185°.

The selenium was determined by heating the weighed substance with 5 c.c. of fuming nitric acid in a flask with ground-in air condenser. Oxidation being completed, the solution was boiled with excess of hydrochloric acid until all nitrous compounds were destroyed, the metalloid, precipitated as the red modification, transforming into the dark grey variety on warming with sodium sulphite or aqueous sulphurous acid, was collected and weighed. Carbon and hydrogen estimations were made in combustion tubes charged with fine copper oxide, a long length of lead chromate, and a spiral of copper oxide, a little of this oxide being also placed in the porcelain boat. In the combustion of selenium and tellurium derivatives more accurate results were obtained by burning with oxygen alone than with air followed by oxygen (Found, C = 34·23, 33·74; H = 3·45, 3·72; Se = 44·10, 44·17. $(C_5H_6O_2Se)_n$ requires C = 33·86; H = 3·41; Se = 44·68 per cent.).

Molecular determinations by the ebullioscopic method in benzene gave 316, 312 (0·65 and 1·18 grams per 100 c.c. respectively), thus indicating association: $n = 1$ or 2 requires 177 or 354.

Selenium acetylacetone is not obtained unless the prescribed experimental conditions are followed closely in regard to temperature, concentration, proportion of reagents, and removal of the volatile products at the ordinary temperature. The proportion of two molecules of acetylacetone to one of selenium tetrachloride has been found to give the optimum yield, whereas ratios of one or four molecules of the diketone do not give rise to any crystalline product. Experiments carried out in chloroform or with selenium dibromide, Se_2Br_2, and acetylacetone in ether have led so far to elimination of selenium and to the production of lachrymatory oils. A preliminary experiment with benzoylacetone and selenium tetrachloride in cold ether indicated the formation of a pale yellow selenium benzoylacetone (m. p. 212°) having similar properties to selenium acetylacetone.

Selenium acetylacetone, which has a faintly acidic, sweetish taste, dissolves slightly in hot water, the solution being distinctly acid; it is somewhat sparingly soluble in boiling ether, ethyl alcohol, acetone or chloroform, and dissolves more freely in hot glacial acetic acid. Its solubility in boiling benzene is about 1·5 grams in 100 c.c., but is ten times less in the cold.

Selenium acetylacetone dissolves readily in cold aqueous alkali hydroxides or ammonia to bright yellow solutions, which regenerate the compound if neutralised at once with dilute acid. The alkaline solutions speedily decompose, red selenium being precipitated, whilst a nauseating odour is developed. Although insoluble in aqueous sodium carbonate, prolonged treatment with this reagent leads to the foregoing decomposition. The organic product of these alkaline decompositions is an oil having a pleasant ketonic odour.

Dilute mineral acids are without effect on selenium acetylacetone, concentrated nitric and sulphuric acids have a destructive action, whereas cold concentrated hydrochloric acid decomposes it smoothly into red selenium and chloroacetylacetone, identified by its boiling point, lachrymatory properties, and green copper derivative.

Ferric chloride either in aqueous or alcoholic solution gives no red coloration with selenium acetylacetone even after two hours. In twenty-four hours an orange tint is discernible, and this coloration is developed more quickly on boiling, but selenium is set free simultaneously. When distilled with zinc dust, selenium acetylacetone loses selenium, evolves a nauseating vapour, and gives rise to an oil which, after rectification, gives a red coloration with ferric chloride and has a pleasant ketonic odour. Iodine in chloroform solution has no action on selenium acetylacetone, but chlorine in the same solvent gives selenium tetrachloride and chloroacetylacetone, whereas bromine yields lachrymatory products and a colourless, crystalline substance (m. p. 180°). Aqueous hydrogen sulphide decomposes it slowly in the cold with liberation of sulphur and selenium. Hydroxylamine, phenylhydrazine, *p*-bromophenylhydrazine, *p*-nitrophenylhydrazine, and 6-chloro-3:4-tolylenediamine induce a more or less rapid elimination of selenium.

By-products of the Formation of Selenium Acetylacetone.—The amount of hydrogen chloride set free in the condensation was estimated and found to be equivalent to three-fourths of the chlorine originally present in the selenium tetrachloride. The chloroacetylacetone (b. p. 148—150°), of which more than two-thirds of the calculated amount were obtained in a purified condition, was further identified by conversion into its green copper derivative soluble in chloroform. These results support the view expressed by equation 2 (p. 1457).

Quantitative Decomposition of Selenium Acetylacetone: Alkali Selenodithionates.

Two grams of powdered selenium acetylacetone were added to 18 c.c. of water containing 3 grams of potassium metabisulphite ($2\frac{1}{3}$ mols. of $KHSO_3$ equivalent to 1 atom of Se), and the mixture

was shaken mechanically for one hour. A colourless, crystalline precipitate of potassium selenodithionate, $K_2S_2SeO_6$, was then collected, the filtrate extracted with ether to remove acetylacetone, and the aqueous layer mixed with alcohol to complete the deposition of the inorganic product (yield 3·5 grams = 97 per cent. of the theoretical). When separating rapidly from aqueous solution the selenodithionate appeared in lustrous scales or thin plates; when crystallising slowly it was obtained in long, transparent, silky needles.

Both forms of the salt were quite colourless and stable when exposed to air and light. On heating they commenced to redden at 190°, and at 250° the red selenium turned grey. Meanwhile sulphur dioxide was evolved, and finally a residue of potassium sulphate was left (Found, K = 24·59; S = 20·06, 20·58; Se = 25·06, 25·07. Calc., K = 24·63; S = 20·19; Se = 24·95 per cent.).

Sodium selenodithionate, $Na_2S_2SeO_6$, was produced by adding selenium acetylacetone to a cold concentrated solution of sodium hydrogen sulphite ($2\frac{1}{3}$ mols.), the mixture being shaken until the organic compound had dissolved, and precipitated, by adding alcohol, in colourless, lustrous anhydrous scales, readily soluble in water (Found, Na = 16·24. $Na_2S_2SeO_6$ requires Na = 16·12 per cent.). Aqueous sulphur dioxide had a similar action on selenium acetylacetone, dissolving it in the cold to a colourless solution containing acetylacetone, extracted by ether, and selenodithionic acid, which slowly decomposed into selenium, sulphur dioxide, and sulphuric acid.

Estimation of Acetylacetone.—The acetylacetone set free in the foregoing decompositions was identified by conversion into its pale blue copper and colourless aluminium derivatives. It was estimated by coupling with sodium *iso-p*-nitrobenzenediazo-oxide.

Selenium acetylacetone (0·2 gram) was shaken for four hours with 0·25 gram of potassium metabisulphite and 3 c.c. of water. Potassium selenodithionate was precipitated by alcohol, and the filtrate treated with 0·23 gram of sodium *iso-p*-nitrobenzenediazo-oxide, ($NO_2 \cdot C_6H_4 \cdot N_2 \cdot ONa, H_2O$). The pale orange-red precipitate of *p*-nitrobenzeneazoacetylacetone, after washing with dilute alcohol, weighed 0·2 gram (calc., 0·28 gram), and gave the correct melting point, 219—222°.

Tellurium acetylacetone dichloride, $C_5H_6O_2{:}TeCl_2$.

Tellurium reacted with dry chlorine, evolving heat and forming tellurium tetrachloride as a yellowish-white liquid, in which excess of the metalloid dissolved to an almost black solution, probably containing the dichloride. With excess of chlorine the whole solidi-

fied to a yellow, crystalline mass of tetrachloride, which was purified by sublimation.

Sublimed tellurium tetrachloride (10·3 grams) was mixed with 7·6 grams of acetylacetone (2 mols.) in 55 c.c. of dry chloroform and the orange solution heated under reflux on the water-bath. The evolution of hydrogen chloride ceased after two hours' boiling; the solution was filtered from a heavy, dark grey oil, and concentrated over lime in a desiccator. Crystals of tellurium acetylacetone dichloride separated; the concentrated filtrates yielded further crops (yield 7 grams, or 62 per cent. calculated on $TeCl_4$). The product was sparingly soluble in ether, benzene, or chloroform, rather more so in hot alcohol, and very readily soluble in cold acetone. It crystallised from alcohol or benzene in acicular forms, and separated slowly from acetone in large, transparent, hexagonal prisms often twinned. Both forms were colourless; they darkened at 155—160° and melted and decomposed between 169° and 173°, liberating tellurium and evolving hydrogen chloride and a lachrymatory oil, which developed a red coloration with aqueous ferric chloride. The tellurium was estimated by warming a weighed amount with fuming nitric acid (5 c.c.) in a reflux apparatus. After boiling with concentrated hydrochloric acid (25 c.c.) to remove nitrous compounds, the solution was evaporated to dryness. The residue dissolved in 15 c.c. of 10 per cent. hydrochloric acid was warmed with 10 c.c. of 15 per cent. hydrazine hydrochloride and 35 c.c. of saturated sulphurous acid gradually added, the liberated tellurium being dried at 107°. The chlorine was estimated by alkaline hydrolysis and precipitation as silver chloride; the combustions were carried out as in the case of selenium acetylacetone (Found, C = 20·72; H = 2·07; Cl = 24·01, 23·95; Te = 42·87. $(C_5H_6O_2Cl_2Te)_n$ requires C = 20·24; H = 2·04; Cl = 23·92; Te = 43·00 per cent.).

Molecular-weight determinations by the ebullioscopic method in acetone (1·846 and 4·207 grams per 100 c.c.) gave 241 and 255 (M = 296·5).

Tellurium acetylacetone dichloride does not become discoloured on exposure to light. It readily loses chlorine with hot water or aqueous acids or alkalis. Tellurium is not set free by boiling with aqueous potassium hydroxide. With aqueous ferric chloride a red coloration is developed only very slowly. When warmed with considerable excess of aqueous sulphurous acid this compound is decomposed completely, yielding tellurium and acetylacetone.

Tellurium Acetylacetone, $C_5H_6O_2$:Te.

The foregoing dichloride (2·2 grams) when triturated for ten minutes with 1·8 grams of potassium metabisulphite (1 mol.) and 20 c.c. of water yielded a small amount of tellurium and 1 gram (yield 60—70 per cent.) of a yellow compound, which was purified by crystallisation from benzene or hot water. This product was also obtained with less liberation of tellurium by boiling the dichloride with a slight excess of aqueous sulphur dioxide (Found, C = 27·14, 26·62; H = 2·88, 2·92; Te = 56·55. $(C_5H_6O_2Te)_n$ requires C = 26·61; H = 2·68; Te = 56·52 per cent.).

Molecular-weight determinations in boiling benzene and acetone (0·462 and 0·879 gram per 100 c.c.) gave respectively 262 and 185. M.W. for $n = 1$ is 225·6.

Tellurium acetylacetone forms heavy, golden-yellow needles sparingly soluble in water, ether, chloroform, or alcohol, and decomposing indefinitely at 145—180°. In a sealed tube it melts to a yellow liquid, which partly sublimes in yellow needles, and on further heating decomposes with elimination of tellurium and production of an oil resembling acetylacetone. Under reduced pressure the compound sublimes at about 160° in glistening, yellow needles.

Tellurium acetylacetone resembles the selenium compound in its chemical reactions. It dissolves in cold aqueous potassium hydroxide to a bright yellow solution, from which immediate neutralisation with acid regenerates the original compound, but after a few minutes the alkaline solution deposits tellurium. Cold concentrated hydrochloric acid decomposes the compound with elimination of tellurium. Ferric chloride develops a red coloration, but only after a long time. Hydrogen peroxide decolorises immediately the yellow aqueous solution of tellurium acetylacetone, giving a white precipitate; hydrogen sulphide produces at once a black deposit (TeS_2 ?), alcoholic mercuric iodide yields a yellow precipitate, and warm aqueous sulphur dioxide reduces the compound with elimination of tellurium.

Quantitative Decompositions of Tellurium Acetylacetone.

(a) *With Bisulphite.*—Tellurium acetylacetone (0·4 gram) shaken for five hours with 0·4 gram of potassium metabisulphite and 3 c.c. of water yielded sulphur dioxide, 0·2 gram of tellurium, and 0·3 gram of potassium sulphate, the latter precipitated by alcohol after extracting the acetylacetone with ether.

Warm aqueous sulphur dioxide brought about a similar reduction, yielding acetylacetone, tellurium, and sulphuric acid.

(b) *With an Aluminium–Mercury Couple.*—Tellurium acetylacetone (0·4 gram) in 50 c.c. of hot water was shaken with an aluminium–mercury couple, and the solution, filtered from precipitated tellurium, was treated with sodium *iso-p*-nitrobenzenediazooxide (0·37 gram) in 8 c.c. of glacial acetic acid and 20 c.c. of absolute alcohol. After three hours the orange-red *p*-nitrobenzeneazoacetylacetone was collected (0·35 gram, yield 80 per cent.) and crystallised from glacial acetic acid; it then melted at 220°.

(c) *With Concentrated Hydrochloric Acid.*—A preliminary experiment showed that tellurium acetylacetone, unlike its selenium analogue, yielded acetylacetone and not chloroacetylacetone on decomposition with concentrated hydrochloric acid, a portion only of the tellurium being precipitated, whilst the remainder was left in solution as tellurium tetrachloride. Tellurium acetylacetone (0·1558 gram) was stirred with cold concentrated hydrochloric acid for several hours. The precipitated tellurium, which was then collected and washed successively with a little more concentrated acid and water, weighed 0·0432 gram. The filtrates were then treated with aqueous hydrazine hydrochloride saturated with sulphur dioxide. These reducing agents precipitated the remainder of the tellurium, which weighed 0·0427 gram (total amount of tellurium found = 0·0859 gram.; calc., 0·0880). These results confirm equation 7 (p. 1459).

The authors desire to express their thanks to the Advisory Council for Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

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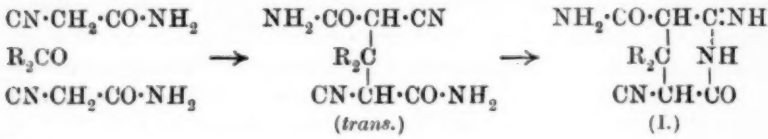
CLXIII.—*The Formation and Reactions of Imino-compounds. Part XX. The Condensation of Aldehydes with Cyanoacetamide.*

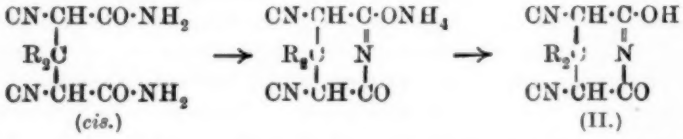
By JAMES NELSON EDMUND DAY and JOCELYN FIELD THORPE.

IN a series of papers dealing with the condensation of ketones with cyanoacetamide (T., 1911, **99**, 422; 1913, **103**, 1586; 1919, **115**, 686) it has been shown that the reaction between these substances in the presence of a condensing agent leads to the formation of *cis-*

and *trans*-additive products, and that ring-formation then ensues, yielding two different types of heterocyclic six-membered systems. Thus the *trans*-condensation proceeds:

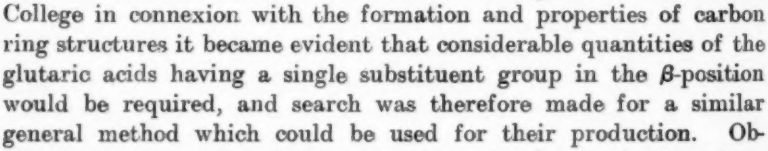


whereas the *cis*-condensation yields:



the compounds formed in this case (II) being the same as those produced by the well-known reaction discovered by Guareschi, which involves the interaction of ethyl cyanoacetate, the ketone, and ammonia. As both types (I) and (II) yield the $\beta\beta$-disubstituted glutaric acid on complete hydrolysis, the method serves as a useful one for the preparation of these important acids in quantity.

In the course of the work which is now being carried out at this College in connexion with the formation and properties of carbon ring structures it became evident that considerable quantities of the glutaric acids having a single substituent group in the β-position would be required, and search was therefore made for a similar general method which could be used for their production. Obviously the use of an aldehyde in place of a ketone in the above reaction suggested itself, but, unfortunately, Guareschi has already shown that, by his method, aldehydes lead to the formation of stable pyridine derivatives which cannot be hydrolysed to the nitrogen-free acid:



(III.)

It was therefore gratifying to find that the condensations between aliphatic aldehydes and cyanoacetamide proceeded very smoothly in the presence of a trace of alkali hydroxide, that yields of 90 per cent. or more were obtained, and that the condensation products could be quickly and completely hydrolysed to the corresponding β-substituted glutaric acid by means of dilute hydrochloric acid.

Moreover, the acids obtained were in a high state of purity and did not require further treatment before use. Evidently, therefore, the method is the best one at present known for the preparation of these acids.

Investigation quickly showed, however, that the condensation products formed in this way were of a different type from those produced in the ketone reactions. They were, for example, insoluble in dilute mineral acids, and were without basic properties. They did not form platinichlorides, and were not hydrolysed to the imide by boiling with mineral acids, a reaction characteristic of the ring imino-compounds of type I. They were, moreover, very much more readily hydrolysed to the nitrogen-free acid than the compounds of either type I or II, and were, in fact, undoubtedly open-chain cyanoamides formed in accordance with the scheme:

$$R\cdot CHO \begin{matrix} CH_2(CN)\cdot CO\cdot NH_2 \\ CH_2(CN)\cdot CO\cdot NH_2 \end{matrix} \longrightarrow R\cdot CH\begin{matrix} CH(CN)\cdot CO\cdot NH_2 \\ CH(CN)\cdot CO\cdot NH_2 \end{matrix}$$

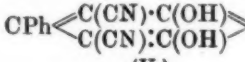
(IV.)

This type of condensation product formed, in every case investigated, approximately 99 per cent. of the total solid obtained. The remainder comprised about equal quantities of the imino-imide of type I and the Guareschi compound of type III.

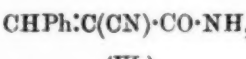
A consideration of these data seems to lead to the conclusion that there is a greater tendency to form six-membered heterocyclic structures when two alkyl groups are attached to the central carbon atom than when only one substituting group is in this position. If this were true and could be applied to homocyclic carbon systems of similar type, it would account for many of the peculiar properties which are possessed by compounds having two alkyl groups attached to the same carbon atom. On the other hand, it is possible that the physical properties of the condensation products may determine the order and amount of their formation. In other words, that whilst the normal compound of type IV is in every case the one first produced, its actual separation as the final product may be influenced by its solubility in the solvent used. Ring-formation may therefore ensue if the solubility of the initial compound prevents it from being removed by precipitation, and if the ring-compound happens to be the less soluble of the two. In support of this view it is to be noted, as already mentioned, that there is definite evidence of ring-formation of both types I and II in the aldehyde condensations. Against it must be placed the fact that, although repeated attempts have been made by varying the solvent,

no variation in the structure of the product has been detected, excepting in the case of benzaldehyde quoted below, which, however, cannot be regarded as being in any way analogous. It is, moreover, significant that in every case investigated the aldehydes gave open-chain amides and the ketones ring-compounds. It is clear that the matter requires further investigation.

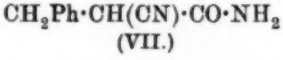
We were unable to induce aromatic aldehydes to yield derivatives of glutaric acid by condensing them with cyanoacetamide. Guareschi, who has applied his reaction to a number of these aldehyes, found that the usual pyridine derivative (V) was formed at the expense of the normal condensation product (VI), which was itself reduced to the substance VII:



(V.)



(VI.)



(VII.)

As a matter of fact the products in the case of benzaldehyde and cyanoacetamide depend on the conditions. Thus, if alcohol is used and a clear solution is maintained throughout, the products V and VII are formed in molecular proportions. If, however, no alcohol is used and the aldehyde is shaken with an aqueous solution of the amide, the sole product is the unsaturated compound (VI). Compound VI is also the sole product if alcohol is used and if the mixture is first seeded with a crystal of the unsaturated amide.

There appears to be no tendency whatever for an aromatic aldehyde to combine with two molecules of cyanoacetamide, and the glutaric acids having an aromatic group in the β-position cannot therefore be prepared by this method.

Experimental.

General Remarks.—Cyanoacetamide was prepared by the method described by Thole and Thorpe (T., 1911, **99**, 429). After recrystallisation from alcohol it was dried in the steam-oven for three hours in order to remove traces of ammonia, a substance which has been found to have a marked hindering effect on condensations of this character.

The condensations were carried out in wide-mouthed, glass-stoppered bottles, the cyanoacetamide being dissolved in five times its weight of water. In some cases in which the heat generated by the reaction necessitated cooling in ice-water, thus causing the precipitation of some cyanoacetamide, a little more water was added in

order to effect complete solution. The aldehydes were fractionated immediately before use and were added to the cooled solution of cyanoacetamide, sufficient alcohol being added, when necessary, to form a clear solution. The condensing agents used were piperidine, diethylamine, and aqueous potassium hydroxide. No difference was noticed between these reagents when comparative experiments were carried out under similar conditions, and, therefore, a small quantity of a 50 per cent. aqueous solution of potassium hydroxide was invariably used.

Acetaldehyde.

αα'-Dicyano-β-methylglutaramide, $CHMe[CH(CN)\cdot CO\cdot NH_2]_2$.—This substance is produced in a yield approximating to 95 per cent. of that theoretically possible when 25·2 grams of cyanoacetamide dissolved in 126 c.c. of water are mixed with 6·6 grams of acetaldehyde and 0·3 c.c. of a 50 per cent. aqueous solution of potassium hydroxide added. Precipitation commences after about ten minutes and is complete at the end of three hours, when the material can be collected. The white, crystalline substance melts in the crude condition at 150—155° to a clear, yellow liquid, but owing to its insolubility it cannot be recrystallised from any of the usual solvents. The specimen for analysis was purified by being first ground with dilute hydrochloric acid and then washed with hot absolute alcohol. It melted sharply at 161° (Found, C = 49·60; H = 5·34; N = 28·92. $C_8H_{10}O_2N_4$ requires C = 49·48; H = 5·19; N = 28·87 per cent.).

β-Methylglutaric Acid.—This acid is produced from the amide in practically quantitative yield when 20 grams of the latter are warmed with 50 c.c. of concentrated hydrochloric acid, and the clear solution, after being diluted with an equal volume of water, is boiled for five hours.

The acid, in a very pure condition, can be extracted from the cooled solution by means of ether, and melts at 87° after being recrystallised from benzene or from dilute hydrochloric acid (Knoevenagel, *Ber.*, 1898, **31**, 2585) (Found, C = 49·17; H = 6·93. Calc., C = 49·3; H = 6·9 per cent. Silver salt, Found, Ag = 59·87. Calc., Ag = 59·95 per cent.).

6-*Imino*-3-*cyano*-5-*carbamyl*-4-*methyl*-2-*piperidone*,

$$CHMe\begin{<}CH(CN)\text{———}CO\\CH(CO\cdot NH_2)\cdot C(:NH)\end{>}NH,$$

can be obtained in small amount (about 0·25 per cent.) when the hydrochloric acid washings from the amide are treated with sodium acetate solution. It separates from water in small, colourless prisms, melts and decomposes at 235°, and is readily soluble in dilute hydrochloric acid. Crystallisation has to be effected rapidly, other-

wise some hydrolysis ensues (Found, C = 49·72; H = 5·39; N = 28·77. $C_8H_{10}O_2N_4$ requires C = 49·5; H = 5·2; N = 28·9 per cent.).

The compound is hydrolysed to β-methylglutaric acid by means of sulphuric acid (compare T., 1911, **99**, 431).

3-Cyano-2 : 6-diketo-4-methylpiperidine-5-carboxylamide,

$$CHMe\begin{<}CH(CN)\text{———}CO\\CH(CO\cdot NH_2)\cdot CO\end{>}NH,$$

is formed by the action of hot dilute hydrochloric acid on the imino-compound (*loc. cit.*). It crystallises from water in colourless prisms which melt and decompose at 245° (Found, N = 21·44. $C_8H_9O_3N_3$ requires N = 21·5 per cent.).

The compound is completely converted into β-methylglutaric acid on hydrolysis with sulphuric acid.

When the original filtrate from the above condensation products is acidified by mixing it with one-third of its volume of concentrated hydrochloric acid a crystalline precipitate is formed which melts after recrystallisation from dilute hydrochloric acid at 252°, decomposing at 255° (Found, N = 24·1. $C_8H_5O_2N_3$ requires N = 24·0 per cent.). The yield of this substance was not more than 0·3 per cent. It is evidently 3 : 5-dicyano-2 : 6-dihydroxy-4-methylpyridine, $CMe\begin{<}C(CN)\cdot C(OH)\\C(CN):C(OH)\end{>}N$, described by Quenda (*Atti R. Accad. Sci. Torino*, 1896—1897, **32**, 415).

Propaldehyde.

αα'-Dicyano-β-ethylglutaramide, $CHEt[CH(CN)\cdot CO\cdot NH_2]_2$.—This substance separates in a crystalline condition when an aqueous solution containing 16·8 grams of cyanoacetamide, 120 c.c. of water, and 5·8 grams of propaldehyde is treated with 0·3 c.c. of a 50 per cent. solution of potassium hydroxide. The yield of the crude product is 90 per cent. of that theoretically possible. When purified by grinding with hydrochloric acid and recrystallisation from a mixture of alcohol and benzene it forms colourless needle clusters which melt at 147°. The compound is insoluble in dilute hydrochloric acid, and is only sparingly soluble in the usual organic solvents (Found: C = 52·67; H = 5·63; N = 26·95. $C_9H_{12}O_2N_4$ requires C = 51·9; H = 5·8; N = 26·9 per cent.).

β-Ethylglutaric Acid.—The above amide is converted into this acid on being boiled for five hours with dilute hydrochloric acid. It melts at 73° after recrystallisation from dilute hydrochloric acid (Emery, *Annalen*, 1897, **295**, 94) (Found, C = 52·71; H = 7·64. Calc., C = 52·5; H = 7·6 per cent. Silver salt, Found, Ag = 57·55. Calc., Ag = 57·7 per cent.).

6-Imino-3-cyano-5-carbamyl-4-ethyl-2-piperidone,

$$CHEt\begin{matrix}CH(CN)\text{———}CO\\CH(CO\cdot NH_2)\cdot C(:NH)\end{matrix}NH,$$

occurs to the extent of about 0·5 per cent. in the original condensation, and can be isolated from the hydrochloric acid washings from the main product on treatment with aqueous sodium acetate. It separates from water in small crystals melting and decomposing at 214° (Found, N = 26·86. $C_9H_{12}O_2N_4$ requires N = 26·9 per cent.).

The compound is readily soluble in dilute hydrochloric acid.

3-Cyano-2 : 6-diketo-4-ethylpiperidine-5-carboxylamide,

$$CHEt\begin{matrix}CH(CN)\text{———}CO\\CH(CO\cdot NH_2)\cdot CO\end{matrix}NH,$$

is produced in a crystalline condition when the above piperidone base is dissolved in dilute hydrochloric acid and the solution boiled for a few minutes. It separates in small, colourless prisms which, when recrystallised from water, melt and evolve gas at 236° (Found, N = 20·06. $C_9H_{11}O_3N_3$ requires N = 20·1 per cent.).

Both the above compounds are converted into β-ethylglutaric acid on hydrolysis.

n-*Butaldehyde.*

αα'-Dicyano-β-propylglutaramide, $CHPr^n[CH(CN)\cdot CO\cdot NH_2]_2$.—A yield of this substance representing 90 per cent. of that theoretically possible is produced when a solution containing 25·2 grams of cyanoacetamide, 180 c.c. of water, and 10·8 grams of *n*-butaldehyde is treated with 0·3 c.c. of an aqueous solution of potassium hydroxide. Precipitation is complete inthe course of three hours, and purification can be effected by grinding with dilute hydrochloric acid and crystallising from a mixture of alcohol and benzene. It forms a white, microcrystalline powder which melts at 136° (Found, C = 54·17; H = 6·30; N = 25·35. $C_{10}H_{14}O_2N_4$ requires C = 54·00; H = 6·4; N = 25·2 per cent.).

The compound is insoluble in hydrochloric acid.

β-Propylglutaric Acid, $CHPr^n(CH_2\cdot CO_2H)_2$.—The hydrolysis of the amide (25 grams) is best effected by means of a solution containing 70 c.c. of concentrated hydrochloric acid diluted with 100 c.c. of water, and is complete after having been boiled for five hours. The acid can be isolated by extraction with ether and purified by recrystallisation from hydrochloric acid, when it is obtained in small, needle-shaped crystals melting at 52° (Found, C = 55·04; H = 8·22. $C_8H_{14}O_4$ requires C = 55·2; H = 8·1 per cent.).

The acid is freely soluble in all the usual organic solvents and

in water. The *silver* salt is a white, apparently amorphous powder (Found, Ag = 55·55. $C_8H_{12}O_4Ag_2$ requires Ag = 55·6 per cent.).

The *anhydride*, $CHPr<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>O$, prepared from the acid through the agency of acetyl chloride, is a colourless, mobile liquid boiling at 180°/20 mm. (Found, C = 61·24; H = 7·68. $C_8H_{12}O_3$ requires C = 61·5; H = 7·8 per cent.).

The *semianilide*, $CHPr^{\alpha}(CH_2\cdot CO\cdot NHPh)\cdot CH_2\cdot CO_2H$, from a benzene solution of the anhydride and aniline, crystallises from benzene in small, colourless plates melting at 128° (Found, N = 5·86. $C_{14}H_{19}O_3N$ requires N = 5·6 per cent.).

The *diethyl* ester, $CHPr^{\alpha}(CH_2\cdot CO_2Et)_2$, prepared from the acid by means of alcohol and sulphuric acid, is a colourless oil which boils at 132°/10 mm. (Found, C = 62·81; H = 9·62. $C_{12}H_{22}O_4$ requires C = 62·6; H = 9·6 per cent.).

6-*Imino*-3-*cyano*-5-*carbamyl*-4-*propyl*-2-*piperidone*,

$$CHPr^{\alpha}<\begin{matrix}CH(CN)\text{———}CO\\CH(CO\cdot NH_2)\cdot C(:NH)\end{matrix}>NH.$$

—This substance is precipitated in a crystalline condition when the hydrochloric acid washings from the amide (p. 1471) are treated with sodium acetate solution. It separates from alcohol in small, prismatic crystals melting and decomposing at 208° (Found, N = 25·95. $C_{10}H_{14}O_2N_4$ requires N = 25·2 per cent.).

The compound is readily soluble in dilute hydrochloric acid.

3-*Cyano*-2:6-*diketo*-4-*propylpiperidine*-5-*carboxylamide*,

$$CHPr^{\alpha}<\begin{matrix}CH(CN)\text{———}CO\\CH(CO\cdot NH_2)\cdot CO\end{matrix}>NH,$$

separates, on cooling, from a solution of the piperidone derivative in dilute hydrochloric acid after it has been boiled for five minutes. It separates from water in small, colourless needles melting at 229° with effervescence (Found, N = 18·62. $C_{10}H_{13}O_3N_3$ requires N = 18·8 per cent.).

The two last-named substances are each converted into β-propylglutaric acid on complete hydrolysis with sulphuric acid.

Benzaldehyde.

The conditions governing the course of the reaction between cyanoacetamide and benzaldehyde are discussed on p. 1468. The practical details are as follows.

(1) *Condensation in the Presence of Alcohol without Seeding.*—Cyanoacetamide (25 grams) dissolved in 126 c.c. of water is mixed with 16 grams of benzaldehyde and sufficient alcohol added (usually

about 90 c.c.) to give a clear solution. The addition of the usual amount of concentrated aqueous potassium hydroxide failed to produce any precipitation, and the solution was therefore kept for three days at 38—40°. Extraction with ether then yielded a solid material which crystallised from dilute alcohol in needles melting at 129—130° (Found, C = 68·77; H = 5·80; N = 16·29. Calc., C = 68·9; H = 5·7; N = 16·1 per cent.).

The compound was proved to be identical with α-cyano-β-phenylpropionamide, $CH_2Ph{\cdot}CH(CN){\cdot}CO{\cdot}NH_2$, by direct comparison with a specimen of this substance prepared by Hessler's method (*Amer. Chem. J.*, 1899, **22**, 169) by the action of benzyl chloride on the dry sodium compound of ethyl cyanoacetate.

When the aqueous solution left after extraction with ether in the above experiment is acidified with hydrochloric acid a white precipitate is formed, which crystallises from alcohol or, better, from dilute hydrochloric acid in needle clusters melting and decomposing at 245° (Found, C = 65·6; H = 3·28; N = 17·93. Calc., C = 65·8; H = 2·9; N = 17·7 per cent.). The compound is evidently 3:5-dicyano-6-hydroxy-4-phenyl-$\Delta^{3,6}$-dihydro-2-pyridone,

$$CPh\begin{matrix}C(CN)\text{———}CO\\ CH(CN){\cdot}C(OH)\end{matrix}N,$$

originally prepared by Guareschi (*Atti R. Accad. Sci. Torino*, 1898—1899, **34**, 565) by the action of ammonia on a mixture of benzaldehyde and ethyl cyanoacetate. Guareschi describes his compound as crystallising with $3H_2O$, but a direct comparison of the two compounds left no doubt as to their identity. The substance is remarkable in that it is freely soluble in cold water and will crystallise from this solvent in the hydrated form described by Guareschi if the solution is sufficiently concentrated.

If, however, a small quantity of hydrochloric acid is added to the aqueous solution, the compound immediately separates in the anhydrous condition. The relative amounts of the two compounds formed in the above condensation are approximately in the proportion of their molecular weights, namely, 10 grams of the amide to 16·5 grams of the pyridine derivative.

(2) *Condensation without Alcohol.*—The same quantities were used as in the previous experiment, only in this instance no alcohol was added. Vigorous shaking was necessary in the initial stages of the reaction, but the condensation product soon began to form, and the precipitation was complete after two hours. The compound produced in this way crystallised from benzene in clusters of silky needles melting at 123° (Found, C = 69·55; H = 4·73; N = 16·63.

Calc., C=69·7; H=4·7; N=16·3 per cent.), and was proved by direct comparison to be α-cyanocinnamamide,

$$CHPh{:}C(CN)\cdot CO\cdot NH_2,$$

and to be the same substance as that prepared by Heuck (*Ber.*, 1895, **28**, 2252).

(3) *Condensation in the Presence of Alcohol with Seeding.*—A yield of 80 per cent. of α-cyanocinnamamide in a pure, crystalline condition can be obtained in the course of two hours when a solution containing 16 grams of cyanoacetamide, 21 grams of benzaldehyde, 70 c.c. of alcohol, and 84 c.c. of water, which has been mixed with 0·3 c.c. of a 50 per cent. solution of potassium hydroxide in water, is seeded with a crystal of the unsaturated amide.

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SOUTH KENSINGTON. [*Received, October 26th*, 1920.]

CLXIV.—*The Constitution of Polysaccharides. Part I. The Relationship of Inulin to Fructose.*

By JAMES COLQUHOUN IRVINE and ETTIE STEWART STEELE.

IT has been shown by one of us in the course of previous publications* that a general method for determining the structure of both di- and poly-saccharides is opened out through the constitutional study of methylated sugars.

Although the programme of research contemplated in this laboratory has been definitely stated on more than one occasion, we are aware of the fact that other workers have entered this field. It is thus necessary again to point out that the systematic investigations on methylated sugars which have been carried out here for the past twenty years were conducted essentially with the object of rendering possible the extension of our work on obvious lines to the more attractive problems presented by the complex carbohydrates. The preparation of as large a variety as possible of alkylated aldoses and ketoses, and the elucidation of their structure, provided, for purposes of identification, the substances which we anticipated would be encountered in solving the constitution of the compound sugars.

The principle involved is a simple one, in that it is generally possible to substitute all the free hydroxyl groups in a carbohydrate or its derivatives by stable methoxyl groups, and sub-

* References to the use of alkylated sugars are given in the bibliography attached to "The Simple Carbohydrates and the Glucosides" (E. F. Armstrong, 3rd edition), and the principles involved are fully described in the *Biochemische Zeitschrift*, 1909, **22**, 357.

sequent hydrolysis yields a methylated sugar or sugars. Determination of the number and position of the alkyl groups in each of the hydrolytic products thus gives direct evidence as to the linkage of the constituents in the parent complex. The general method has already been applied in this laboratory to the constitution of natural and synthetic glucosides (Purdie and Irvine, T., 1903, **83**, 1021; Irvine and Rose, T., 1906, **89**, 814), to disaccharides (Purdie and Irvine, *loc. cit.*, and T., 1905, **87**, 1022; Irvine and Dick, T., 1919, **115**, 593; Haworth and Law, T., 1916, **109**, 1314; Haworth and Leitch, T., 1919, **115**, 809), and also to a typical polysaccharide (Denham and Woodhouse, T., 1913, **103**, 1735; 1914, **105**, 2357).

Recent developments in the chemistry of the sugars have added greatly to the complexities involved, and, incidentally, have furnished ample justification of the policy which restrained us from the premature study of the polysaccharides. It is now recognised that a hexose can react, not only as a butylene-oxide, but also in the more reactive forms, provisionally termed "γ-sugars" (Fischer, *Ber.*, 1914, **47**, 1980; Irvine, Fyfe, and Hogg, T., 1915, **107**, 524; Irvine and Robertson, T., 1916, **109**, 1305; Cunningham, T., 1918, **113**, 596). The chief weight of evidence is in favour of the idea that these isomeric forms of the hexoses possess an ethylene-oxide structure, but no rigid formula can yet be applied to all examples, and the possibility that an aldo-hexose may react as a propylene-, amylene-, or hexylene-oxide must also be kept in view. Evidently the constituent sugars of a di- or poly-saccharide may be present in any of the structural forms mentioned above, and thus the evidence afforded by the hydrolysis of the unsubstituted complex may be misleading. The case of sucrose may be quoted in illustration. The sugar, on hydrolysis, yields glucose and fructose of the ordinary type, but it has been shown from the study of octamethyl sucrose that the fructose constituent is present in the "γ-form" (Haworth and Law, *loc. cit.*).

It follows that the complete constitution of a compound sugar, from the disaccharides up to the polysaccharides, must include the identification of (1) the constituent sugars, (2) their stereochemical form (α or β), (3) the hydroxyl groups involved in the coupling of the constituents, and (4) the position of the internal oxygen ring in each sugar. Determination of factors (3) and (4) demands the introduction of non-hydrolysable residues into the molecule, and it is in this connexion that alkylated sugars play their most useful part.

Taking the above considerations into account, we have resumed

the study of the constitution of cellulose, and have also extended our work to starch and inulin, the results obtained in the last example being now submitted.

The experimental methods employed follow closely the lines already laid down in the methylation of cellulose. It will be recalled that, by subjecting cotton cellulose to the action of methyl sulphate and sodium hydroxide solution, Denham and Woodhouse (*loc. cit.*) obtained a substance possessing the composition of a trimethyl cellulose, from which they isolated a well-defined, crystalline trimethyl glucose as one of the hydrolytic products. The research in question is important, as it showed that complete methylation can be effected by means of methyl sulphate in cases where the insolubility of the carbohydrate under examination prohibits the use of methyl iodide and silver oxide as the methylating reagents.

Although inulin, as the most widely distributed reserve material derived solely from fructose, is a compound of considerable importance, nothing is known regarding its exact constitution beyond the fact that it is non-reducing and yields fructose on hydrolysis. Even the question of its empirical composition has been debated, as the results of elementary analysis do not agree exactly with the figures required for a compound, $(C_6H_{10}O_5)_x$. A review of the literature shows that these variations in composition are small, and are doubtless to be attributed to imperfect washing of the samples and the method of drying adopted. It is now shown that inulin, purified and dehydrated as described in the experimental part, is essentially a polyanhydrofructose with the formula given above. This view does not ignore the presence of the small quantities of inorganic constituents usually associated with inulin, the removal of which is so difficult as to suggest that they form a minute, but definite, part of the molecular complex.

As it is possible that, in the past, several closely related polysaccharides have been included under the general name of *inulin*, it is necessary to specify the origin and treatment of the material used in the course of the present research. The inulin employed was prepared from dahlia tubers, the standards of purity adopted being that the compound should be white, should give less than 0·2 per cent. of ash on ignition, be free from any action on Fehling's solution, and display the constant specific rotation of $-35{\cdot}0°$ on successive "crystallisation" from water.

So far as the methylation process is concerned, inulin possesses a marked advantage over cellulose or starch in that it is soluble in aqueous sodium hydroxide. When this solution was treated with methyl sulphate, methylation proceeded normally, but did not

extend beyond the stage at which *dimethyl inulin* was the essential product. A second treatment with the methylating mixture had very little effect on the methoxyl content of the syrup thus obtained, and, judging from the consistent physical constants displayed by the product of different preparations, it was evident that dimethyl inulin, $[C_6H_8O_3(OMe)_2]_x$, is a definite compound. In order to substitute the remaining hydroxyl group, recourse was had to the silver oxide method of alkylation. Dimethyl inulin mixes freely with methyl or ethyl alcohols, giving a colloidal solution, which is not coagulated by the addition of methyl iodide. By warming such a solution with silver oxide, further methylation was effected, but the process was tedious, owing to the colloidal nature of the material being manipulated. The final alkylations were, as usual, conducted in methyl iodide solution, and in this way *trimethyl inulin*, $[C_6H_7O_2(OMe)_3]_x$, was obtained. It was not found possible to increase the methoxyl content beyond this stage, a result which shows that the series of processes did not result in appreciable degradation, hydrolysis, or oxidation of the polysaccharide. Trimethyl inulin is a viscous, colourless syrup, soluble in organic solvents generally, and behaving like a glucoside towards Fehling's solution. The compound could not be crystallised, and although in small quantities it may be distilled from a metal-bath at 196°/0·15 mm., the process is wasteful, and the further examination was conducted on undistilled material. As in the case of dimethyl inulin, there can be little doubt that the substance is a definite chemical individual, the product of different preparations, in which the experimental procedure was varied, showing identical physical constants. It is important to note the marked alteration in optical activity which occurs during successive methylation. Whereas dimethyl inulin, like inulin itself, is lævorotatory, the introduction of a third methyl group alters the sign, and trimethyl inulin is dextrorotatory ($[\alpha]_D^{15} + 55{\cdot}6°$ in chloroform).

On hydrolysis, by heating at 100° with 1 per cent. oxalic acid, trimethyl inulin was converted into *trimethyl fructose*, the polarimetric record of the change showing a smooth, unbroken curve. When the methylated ketose was isolated and purified by vacuum distillation, it was at once evident that the product belonged to the γ-series. The sugar was dextrorotatory ($[\alpha]_D^{15} + 30{\cdot}5°$ in water), reduced potassium permanganate instantaneously in the cold, and also, although more slowly, Fehling's solution and an ammoniacal solution of silver nitrate. As this is the first occasion on which a trimethyl γ-fructose has been obtained, it was necessary, for the purposes of identification, to convert the compound into a

methylated sugar already known and characterised. This was effected by condensing the compound at 30° with methyl alcohol containing 0·25 per cent. of hydrogen chloride and methylating the trimethyl γ-methylfructoside thus produced by means of the silver oxide reaction. It is to be noted that the above process gives a mixture, in unknown proportions, of the α- and β-forms of tetramethyl γ-methylfructoside, so that direct comparison with other preparations of the same compound was at this stage impossible. By hydrolysis, however, tetramethyl γ-fructose was produced, and this proved to be identical with the form of tetramethyl fructose isolated from sucrose (*loc. cit.*). As the sugar is a liquid, and, so far as known, gives no crystalline derivatives, the identification rests primarily on the physical constants determined. These are quoted in the following table and compared with the values given by the two forms of tetramethyl fructose already known.

Comparison of Tetramethyl Fructoses.

A.	*B.*	*C.*	
From inulin.	From sucrose.	From β-methyl-fructoside.	
Liquid, b. p. 148·5°/10 mm.	Liquid, b. p. 154°/13 mm.	Solid, m. p. 98—99°	
n_D^{15} 1·4554.	n_D 1·4545.	—	
$[\alpha]_D^{15}$ (permanent) +15·5°...	+14·04°	−20·2°	in ethyl alcohol
,, +32·99°..	+31·7°	−20·9°	in water.
Reduces $KMnO_4$.	Reduces $KMnO_4$.	Stable towards $KMnO_4$.	

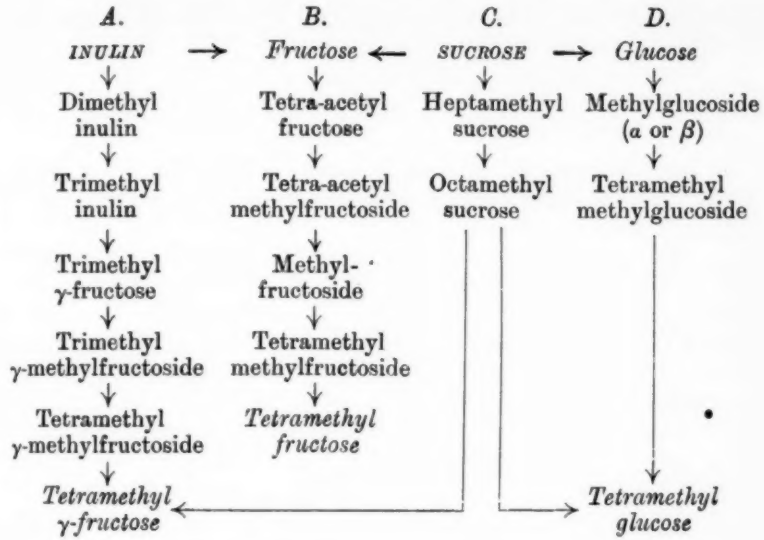
There can be no doubt as to the identity of products *A* and *B* and their differentiation from *C*. In confirmation, samples of tetramethyl γ-fructose from inulin and from sucrose were dissolved in methyl alcohol containing 0·25 per cent. of hydrogen chloride, and the changes in rotation observed at frequent intervals as the formation of the corresponding methylfructoside proceeded. The speed of reaction in these parallel experiments was identical at 30°, and the end-points coincided, thus confirming the identity of the sugars used.

Discussion of Results.

The bearing of our combined results on the constitution of inulin may be seen from a survey of the reactions described in the present and related researches (p. 1479).

In series *A* and *C*, the γ-fructose component remains throughout in the γ-form, whilst in *B* and *D* the stable types alone are operative.

It is evident from the above that the structural relationship



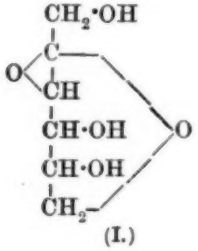
between sucrose and inulin is a close one. Both compounds are non-reducing, undergo hydrolysis with extreme ease, and, under ordinary conditions, yield the form of fructose melting at 112—114° and displaying $[\alpha]_D^{15} - 93°$ after mutarotation. We have carried out test hydrolysis of the inulin used in our experiments, and were able to isolate a yield of 66 per cent. of the theoretical amount of crystalline fructose showing the above constants. This result is, however, utterly misleading from the structural point of view, as the fructose component is present in the isomeric γ-form. Moreover, the yields obtained in the first three stages of *A*, and the complete uniformity of the tetramethyl fructoses produced in processes *A* and *C*, show that *all the fructose residues in inulin belong to the γ-series.* Again, the hydrolysis of trimethyl inulin gives an excellent yield of trimethyl fructose, the weight of lower-boiling distillate then isolated being less than 4 per cent. of the material treated. This leads to the second conclusion, that *inulin is an aggregate of γ-fructose residues, each ketose molecule having lost two hydroxyl groups in the formation of the polysaccharide.* If this were not the case, the hydrolysis of trimethyl inulin would have given a mixture of sugars ranging from dimethyl to tetramethyl fructoses in place of a trimethyl fructose alone.

The above conception admits of two interpretations. According to one alternative, the polysaccharide may be regarded as a polymerised anhydro-γ-fructose, in the formation of which the reducing

group of the fructose residue takes part in the dehydration, and is thus eliminated.

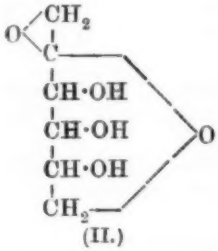
$$\underset{\gamma\text{-Fructose.}}{C_6H_{12}O_6} \longrightarrow C_6H_{10}O_5 \longrightarrow \underset{\substack{\text{Polymerised anhydro-}\\ \gamma\text{-fructose.}}}{(C_6H_{10}O_5)_x}$$

The combined results of several researches, so far unpublished, show that the most probable formula for anhydro-γ-fructose is either



(I.)

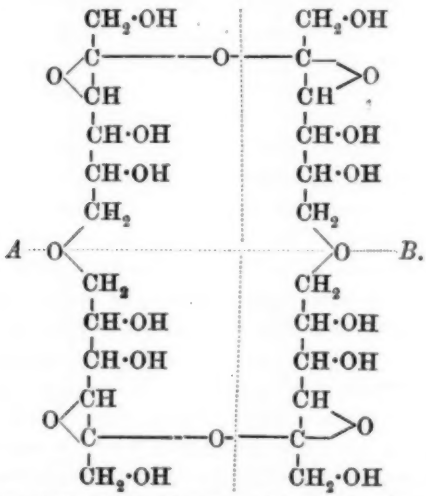
or



(II.)

Both structures admit of polymerisation, on the lines suggested by Pictet and his collaborators, to give a complex carbohydrate, and although the formulæ need not be further discussed at this stage, it may be mentioned that I is regarded as more probable than II.

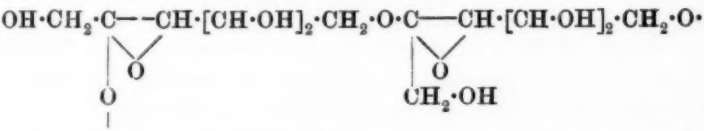
The alternative view of the structure of inulin involves the idea that γ-fructose molecules are condensed together in such manner that each ketose component loses two hydroxyl groups, one of which is the reducing group, in the condensation.



(The dotted lines indicate the cleavage of the molecule on hydrolysis.)

In order to satisfy all the conditions, including the fact, now established, that *inulin contains three hydroxyl groups in each unit of six carbon atoms*, the number of ketose residues necessary to form a symmetrical molecule must be a multiple of two. The physical properties of inulin show that the compound is not a disaccharide, and, taking the next simplest case, our results would be explained by the formula shown on p. 1480, which permits of expansion to a hexa- or octa-saccharide by the addition of coupled ketose residues at the etheric linkages marked *A* and *B*.

The formula on p. 1480, equally with the first alternative discussed, involves that in each C_6 unit of inulin the same hydroxyl groups are unsubstituted, and that two of these groups are different from the third. This is consistent with the methylation of the compound in definite steps. It also demands that only one form of trimethyl fructose should be produced from trimethyl inulin, and this is again in agreement with the experimental evidence. The formula suggested is, of course, capable of considerable modification, as any part of the carbohydrate chain may be lengthened by coupling the reducing group of one ketose residue with one of the primary alcohol groups of the next. Part of the inulin molecule would, in such case, contain the system



It is, of course, unlikely that inulin possesses a structure so simple as that of a tetrasaccharide, but the fact that trimethyl inulin is perceptibly volatile at 196°/0·15 mm. suggests that the molecular weight of the polysaccharide is much smaller than is generally imagined to be the case. The high molecular weights quoted in the literature are discordant, and can have little significance.

At the present stage it is premature to give a decided opinion on the relative merits of the two alternative formulæ for inulin now proposed, and the research is being continued. It is also our intention to attempt the synthesis of sucrose from the form of fructose now shown to be present in inulin.

Experimental.

Purification of Inulin.

Crude inulin prepared from dahlia tubers was boiled with charcoal until colourless, and separated from the filtrate by freezing.

Thereafter, the material was "recrystallised" several times until the action on Fehling's solution had entirely disappeared, after which it was transferred to tall cylinders and shaken with cold distilled water. When the inulin settled, the wash-water was syphoned off and the treatment repeated, the process being continued for a week. This method of washing proved to be quite as effective as dialysis in yielding a product giving the minimum of ash on ignition.

After filtration, the moist inulin was spread on plates to ensure that uniform hydration was obtained before commencing the drying process. In this condition, the material contained 60 per cent. of water, and in quantities of 200 grams was shaken with 25 per cent. aqueous alcohol. After settling, the dilute alcohol was poured away, and 50 per cent. alcohol substituted. This, in turn, was successively replaced by 84, 95, and 98 per cent. alcohol. Exactly similar treatment was then given with mixtures of absolute alcohol and ether until, finally, pure ether was used as the washing agent. After filtration, the inulin was kept in a high vacuum until constant in weight. This somewhat elaborate method of dehydration appears to be necessary in order to obtain inulin as a fine, white mass of uniform microscopic appearance. The compound was dried at 50°/80 mm. over phosphoric oxide, but it was found that, owing to surface attraction of moisture, it was extremely difficult to obtain constant weighings. A dry sample gave, for $c = 2{\cdot}7624$, $[\alpha]_D^{15} - 34{\cdot}21°$ in water.

Hydrolysis of Inulin.

This reaction was repeated, for reasons stated in the introduction. Using Wohl's method (*Ber.*, 1890, **23**, 2107), in which inulin is heated with very dilute hydrochloric acid, the yield of solid fructose varied considerably, but the average result of a series of experiments was that 200 grams of dry inulin gave directly 45 grams of crystalline fructose, and a further 11·5 grams were obtained from the syrupy by-products.

On the other hand, when the hydrolysis was effected by dilute oxalic acid, the proportion of crystalline fructose was greatly increased, the mean result being a yield of 132 grams of crystallisable sugar from 200 grams of inulin.

Preparation of Dimethyl Inulin.

As the methylation of inulin presents some unusual features, an account is given of a typical experiment. Thirty-two grams of finely powdered pure inulin (2 mols.) were dissolved in 40 c.c. of

45 per cent. sodium hydroxide by heating in water at 60—70°, and, after cooling, 80 c.c. of methyl sulphate (3 mols.) and 140 c.c. of 50 per cent. sodium hydroxide (total, 6 mols.) were run simultaneously into the solution, which was maintained at 35°. This addition extended over three hours, the mixture meanwhile being vigorously stirred and the alkali kept in excess. Thereafter, the temperature was slowly raised to 75°, and finally to 100°, for thirty minutes. Carbon dioxide was then passed through the liquid for a prolonged period in order to destroy the bulk of the sodium hydroxide, and, without removing the suspended solids, an approximately equal volume of 88 per cent. alcohol was added. After again passing carbon dioxide and allowing to stand, a further quantity of inorganic salts was deposited. These were separated by filtration, drained, and washed with rectified spirit. Dilute sulphuric acid was then added to the filtrate until it was exactly neutral, when the aqueous alcohol was distilled off under diminished pressure. The bulk of the product was contained in the residue, but some remained behind with the inorganic salts, so that both portions were extracted several times with boiling absolute alcohol. This solvent, however, takes up sodium methyl sulphate, which is formed in considerable amount as a by-product of the reaction, and consequently an extraction with boiling chloroform was carried out, thus leaving the sodium salt undissolved. On concentration, an amber-coloured syrup was obtained, which was subjected to a second methylation. The same proportions of reagents were used, and the crude syrup was isolated in the manner just described. Thereafter, it was further purified by boiling repeatedly with ether to dissolve any methylated fructose which might have been formed, owing to hydrolysis. The undissolved syrup was then boiled in chloroform solution for three hours with decolorising charcoal. The clarified solution, when dried over magnesium sulphate, gave, on removal of the solvent, a clear, amber syrup, amounting to 78 per cent. of the weight of inulin taken. This, on further drying in a vacuum-oven at 100°, became so brittle that it could be powdered (Found: C = 50·55; H = 7·51; OMe = 35·8; ash = 1·76. $[C_6H_8O_3(OMe)_2]_x$ requires C = 50·53; H = 7·37; OMe = 32·7 per cent.).

Dimethyl inulin, although sparingly soluble in cold water, gives a faintly opalescent solution in hot water. The aqueous solution behaved as a glucoside towards Fehling's solution and reduced aqueous potassium permanganate rapidly, but not so quickly as a true γ-sugar.

For $c = 1·845$, $[\alpha]_D^{15} - 42·1°$ in chloroform.

Preparation of Trimethyl Inulin.

In the further methylation of dimethyl inulin, it was found necessary to adjust the procedure according to small variations in the composition of the material used. When the methoxyl content corresponded exactly with that required for a dimethyl inulin, the compound gave a clear solution in methyl iodide. The presence, however, of even small quantities of lower methylated compounds affected this solubility to such an extent that the addition of methyl alcohol was necessary. In this event, the alkylation was conducted in methyl-alcoholic solution by the addition of methyl iodide, and subsequently silver oxide, the process being repeated until the product was freely soluble in methyl iodide alone. The final alkylation was then carried out in the absence of any extraneous solvent.

On the other hand, when a methylated inulin contained more than 32 per cent. of methoxyl, the compound was soluble in methyl iodide, and one methylation was then sufficient to give a trimethyl inulin. Twenty-five grams (1 mol.) of dimethyl inulin were dissolved in 100 grams of methyl iodide at the boiling point. When a clear solution was obtained, 63 grams (2 mols.) of silver oxide were gradually added, and the alkylation continued by boiling under reflux for eight hours. The product was isolated by extracting with hot alcohol, the solvent removed, and the residue extracted with a large excess of boiling ether. The ethereal solution was heated with charcoal to remove traces of dissolved silver, dried over anhydrous sodium carbonate, and the solvent removed, leaving a clear, viscous syrup. Even after two further methylations in methyl iodide solution, the methoxyl content did not increase above the value quoted below, so that the formation of trimethyl inulin represents the limit of the reaction. The complete drying of the product presented difficulties. When heated at 80°/8 mm., the syrup darkened and developed acidity, which resulted in hydrolysis. It was thus necessary to dehydrate the material slowly at 65°/150 mm. (Found: C=53·05; H=7·64; OMe=43·83. $[C_6H_7O_2(OMe)_3]_x$ requires C=52·94; H=7·84; OMe=45·5 per cent.).

Trimethyl inulin is a colourless syrup resembling in appearance anhydrous glycerol at 10°. The compound mixes freely with alcohol, chloroform, or acetone, but is sparingly soluble in ether or in water. A significant fact is that solution of methylated inulin in organic solvents removed all associated mineral matter, so that the compound then left no ash on ignition. Trimethyl inulin has no effect on boiling Fehling's solution, but, like the parent

polysaccharide, is very readily hydrolysed by heating with dilute acids, and it is likewise unaffected by potassium permanganate solution. No crystallising medium could be found for the compound, and it is doubtful if it forms true solutions in any solvent.

For $c=1{\cdot}980$, $[\alpha]_D^{15}+55{\cdot}6°$ in chloroform; $c=1{\cdot}3707$, $[\alpha]_D^{15}+50{\cdot}34°$ in ethyl alcohol.

Experiments on a small scale showed that trimethyl inulin can be distilled under low pressures, but the process is wasteful, owing to the ready tendency of the compound to generate traces of organic acids. This occasions some hydrolysis, and trimethyl γ-fructose thus contaminates the distillate. The first material to distil boiled at 126—132°/0·15 mm., was acid to litmus, and reduced Fehling's solution in the cold. These properties, together with the mobility of the syrup and its action on potassium permanganate solution, which it reduced instantaneously, showed that the product was trimethyl γ-fructose (Found: OMe=42·92. Calc.: OMe=41·88 per cent.).

For $c=2{\cdot}58$, $[\alpha]_D^{15}+31{\cdot}01°$ in ethyl alcohol.

The fraction of higher boiling point (b. p. 196°/0·15 mm.) was a viscous syrup soluble in water and organic solvents generally. Although the material effected some reduction of Fehling's solution on heating, the behaviour of the compound towards this reagent was essentially that of a glucoside (Found: C=51·09; H=7·62; OMe=41·8. $[C_6H_7O_2(OMe)_3]_x$ requires C=52·94; H=7·84; OMe=45·5 per cent.).

The lack of exact agreement with the calculated figures is readily explained by the presence of a small quantity of dimethyl fructose, and the properties of the distillate show that this is the case. The compound was slowly hydrolysed at 15° by *N*/10-hydrochloric acid, the specific rotation falling during the reaction to +42·4°. Recalculation of the end-value for the weight of hexose formed gives $[\alpha]_D^{15}+37{\cdot}8°$, which is in fair agreement with the rotatory power of trimethyl γ-fructose.

Hydrolysis of Trimethyl Inulin. Trimethyl γ-Fructose.

A 10 per cent. solution of undistilled trimethyl inulin in 1 per cent. aqueous oxalic acid was heated at 100°, the progress of the hydrolysis being ascertained polarimetrically. The optical changes observed were regular, the specific rotation diminishing from +53·5° to 40·9° in eight hours. After neutralising the solution with calcium carbonate, the filtrate was decolorised with charcoal and evaporated to dryness under diminished pressure. The residue was extracted with ether, the solution dried over

anhydrous sodium carbonate, and the solvent removed. A colourless syrup then remained, which was distilled under diminished pressure.

A small first fraction was collected at 127—129°/0·25 mm., but the main fraction, which weighed 76 per cent. of the trimethyl inulin taken, boiled steadily at 146°/0·37 mm. This proved to be trimethyl fructose [Found: C=48·90; H=7·94; OMe=41·49. $C_6H_9O_3(OMe)_3$ requires C=48·75; H=8·11; OMe=41·88 per cent.].

Trimethyl fructose is a viscid syrup resembling glycerol in appearance, and has n_D 1·4689. The aqueous solution reduces neutral potassium permanganate solution instantaneously, and also Fehling's solution in the cold, giving bright red cuprous oxide. Although the sugar likewise reduces ammoniacal silver nitrate at the ordinary temperature, it does not affect mercuric chloride, and fails to give Schiff's reaction. On treatment with phenylhydrazine and acetic acid, it yielded a reddish-brown syrup, which could not be crystallised, and it is impossible to say if the product is a hydrazone or an osazone.

Trimethyl γ-fructose is dextrorotatory in all the solvents examined:

For $c=1·016$, $[\alpha]_D^{15}+30·51°$ in water.
$c=1·029$, $[\alpha]_D^{15}+28·18°$ in ethyl alcohol.
$c=1·052$, $[\alpha]_D^{15}+26·61°$ in chloroform.
$c=1·084$, $[\alpha]_D^{15}+27·77° \longrightarrow +22·14°$ in acetone.

The above optical values were permanent, except in acetone solution, and in this case it would appear that the sugar reacted slowly with the solvent.

This was supported by the observation that when the compound was dissolved in acetone containing 0·05 per cent. of hydrogen chloride, the rotation at first diminished and then increased rapidly until the final value, $[\alpha]_D^{15}+60·0°$, was recorded. This capacity to react with acetone is of importance in giving a clue to the constitution of trimethyl γ-fructose.

Conversion of Trimethyl γ-Fructose into Tetramethyl γ-Methylfructoside.

The formation of the corresponding methylfructoside from trimethyl fructose takes place at the ordinary temperature. A 2 per cent. solution of the sugar in methyl alcohol containing 0·25 per cent. of hydrogen chloride was kept for forty hours at 17°. In this time, the reducing action on Fehling's solution disappeared,

whilst the specific rotation at first diminished and then increased to a constant. The following selected observations show that the speed of condensation is of the same order as that exhibited by γ-fructose derivatives generally.

Time from contact of solvent and solute.	Specific rotation.
1 minute	+18·7°
6 minutes	18·2
60 ,,	24·0
120 ,,	26·1
24 hours	50·3
60 ,,	57·0 (constant)

At 30°, the reaction is much accelerated, and is complete in nine hours. The acid was neutralised by means of silver carbonate, the filtrate evaporated to dryness under diminished pressure, and the residual syrup dissolved in alcohol. After treatment with charcoal to eliminate traces of silver compounds, the solvent was again evaporated, the product extracted with ether, and the extract dried with magnesium sulphate. On removal of the solvent, trimethyl methylfructoside remained as a clear syrup, which, without further purification, was dissolved in methyl iodide (4 mols.) and methylated by the addition of silver oxide (2 mols.). The alkylation was continued for eight hours, and the product was extracted and isolated in the usual manner. On distillation, tetramethyl γ-methylfructoside was obtained as a colourless syrup (b. p. 134—135°/12 mm., n_D 1·4469). After a second methylation under the same conditions, the boiling point was 137—138·5°/12 mm., and refractive index 1·4472. The yield was 80 per cent. of the theoretical amount, and evidence was obtained that the undistillable by-product consisted of a polymerised trimethyl fructose or of a methylated difructose.

The tetramethyl γ-methylfructoside isolated as described was a neutral, colourless syrup which reduced potassium permanganate vigorously. Although the material behaved essentially as a glucoside towards Fehling's solution, some reducing compound (probably tetramethyl fructose) was present, and, as repeated distillation failed to remove this impurity, the analytical figures were affected [Found (after two fractionations): C=52·31; H=8·66; OMe=60·6; n_D 1·4470; (after three fractionations): C=52·33; H=8·47; n_D 1·4471. $C_6H_7O(OMe)_5$ requires C=52·80; H=8·80; OMe=62·0 per cent.].

Considering the method of preparation, two stereoisomerides would be present in unknown proportion, and thus the specific rotation cannot be compared with previous determinations.

For $c=1·192$, $[\alpha]$ +20·98° in ethyl alcohol.

In preparing tetramethyl γ-methylfructoside by the above method, about 20 per cent. of the crude syrup could not be distilled, although the reactions were conducted on trimethyl γ-fructose which had been subjected to repeated distillation. This residue, consisting of a viscous, clear syrup, was further examined. The material was glucosidic, and gave on hydrolysis trimethyl γ-fructose, which was in turn converted into tetramethyl γ-methylfructoside. It would appear that, during the condensation with methyl alcohol, some of the trimethyl γ-fructose had undergone an extraneous change, which is probably auto-condensation or polymerisation.

Tetramethyl γ-Fructose.

The hydrolysis of tetramethyl γ-methylfructoside was carried out in 0·25 per cent. aqueous hydrochloric acid, the concentration of the fructoside being adjusted to 1·0684, so as to render possible comparison with the results obtained in parallel work on the same compound prepared from sucrose.

At the temperature of the room, the reaction was slow and occasioned a fall in rotation. On continuing the hydrolysis at 100°, the activity measured at 15° increased from +24·3° to +30·7° in thirty minutes, but the end-point was difficult to detect, on account of the extreme sensitiveness of the rotation with small fluctuations in temperature. In a control experiment conducted on the same compound derived from sucrose, the permanent value $[\alpha]_D^{15}$ +29·6° was recorded, so that the agreement is close.

The usual procedure was followed in isolating the sugar, which boiled at 148·5°/10 mm. (Found: C=50·88; H=8·57; OMe=53·2; n_D 1·4554. Calc.: C=50·85; H=8·47; OMe=52·5 per cent.; n_D 1·4545).

In every respect, the sugar showed identical properties and physical constants with the tetramethyl γ-fructose obtained from sucrose. After distillation, the compound displayed slight downward mutarotation, the permanent values in water and alcohol, respectively, being $[\alpha]_D^{15}$ +32·9° and 15·5°.

Speed of Condensation of Tetramethyl γ-Fructose with Methyl Alcohol.

The condensation with methyl alcohol was carried out in conjunction with a duplicate experiment in which tetramethyl γ-fructose from sucrose was used. A 1 per cent. solution of the sugar was dissolved in methyl alcohol containing 0·25 per cent. of hydrogen

chloride and preserved at 15°, polarimetric readings being taken at regular intervals. Typical observations are given.

Time from contact of solvent and solute.	Specific rotation.	
1 minute	+26·3°	
4 minutes	21·9	Fall
14 ,,	19·1	
80 ,,	26·3	Rise
1024 ,,	27·9	

Thereafter, the solution was heated at 30—40° to complete the reaction, the end-point being $[\alpha]_D^{15} + 59{\cdot}9°$.

With tetramethyl γ-fructose from sucrose, the minimum rotation recorded is +19·8°, as compared with +19·1° above, whilst the end-point is $[\alpha]_D^{15} + 57{\cdot}6°$, compared with +59·9°. Moreover, on plotting the specific rotations graphically, the curves representing the two parallel reactions were identical within the limits of experimental error.

The above investigation was carried out in connexion with the Carnegie Trust Research Scheme, and we desire to express our thanks to the Trust. We are also much indebted to Professor W. N. Haworth and Mr. J. G. Mitchell for access to results recently obtained by them in the study of the tetramethyl γ-fructose present in sucrose.

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CLXV.—*The Constitution of Polysaccharides. Part II. The Conversion of Cellulose into Glucose.*

By James Colquhoun Irvine and Charles William Soutar.

In the series of investigations on the constitution of polysaccharides with which we are engaged in this laboratory, a prominent place is naturally assigned to the more definite varieties of cellulose. The original literature on the reactions and constitution of cellulose is voluminous, but it cannot be claimed that views regarding even the fundamental nature of the complex are by any means established.

This obscurity is not surprising considering the special difficulties which surround constitutional studies of this type. Even if cellulose can be regarded as a chemical individual in the ordinary sense,

the customary methods of solving problems of structure are of little avail in view of the insolubility of the compound, the dubiety attending its molecular magnitude, its behaviour as a colloid, and the probability that a fibrous structure is not chemically homogeneous. As a result, many of the statements which find a place in the permanent literature are based on very insecure evidence, and are even contradictory. In reviewing briefly the present position of the subject, reference may at this stage be limited to recent papers which have a bearing on fundamental questions.

A normal cotton cellulose is represented by the formula $(C_6H_{10}O_5)_n$, and ideas as to the molecular structure have been formed largely on the evidence afforded by hydrolysis. It is important to note that in this particular case hydrolysis is not readily effected, and involves the use of somewhat drastic reagents, so that taking into account the unstable nature of the hydrolysis products, secondary reactions are inevitable. The fact that numerous and complex degradation compounds are formed has thus given rise to conflicting opinions on the chemical nature of cellulose, but it is unnecessary in the present paper to discuss these rival theories in detail.

Apparently the view which finds most acceptance is that cellulose, like starch, is essentially a polyglucose anhydride, and it may be well to state at once that this conception admits of a double interpretation. The complex may consist of the simple units $C_6H_{10}O_5$ (derived from a hexose by molecular loss of water) polymerised in unknown numbers. On the other hand, n molecules of a hexose may be directly connected together through the elimination of n molecules of water, or, where n is a large factor, of $n-1$ molecules. In either case the first point which must be settled is to ascertain beyond doubt if glucose is actually the hexose formed by the hydrolysis of cellulose, and, if so, to determine exactly the amount of sugar thus produced.

The inquiry becomes much more definite if it can be shown that, within the limits of reasonable experimental error, cellulose can be converted into glucose in terms of the equation:

$$(C_6H_{10}O_5)_n + nH_2O \longrightarrow nC_6H_{12}O_6.$$
$$100 \text{ parts} \longrightarrow 111{\cdot}11 \text{ parts}.$$

From time to time confident statements appear in the literature that practically quantitative yields of glucose have been obtained from cellulose, but the grounds upon which such claims are made are by no means convincing to workers in the sugar group. Practically speaking, the only experimental methods available for degrading cellulose depend upon the use of mineral acids, either alone

or in conjunction with acetic anhydride, and it is evident that any sugar thus liberated must undergo profound alteration when kept in contact with these reagents. This no doubt accounts for the fact that hitherto pure, crystalline glucose has never been obtained from this polysaccharide. Nevertheless, Flechsig (*Zeitsch. physiol. Chem.*, 1883, **7**, 523) claimed that a yield of 95—98 per cent. of the theoretical amount of glucose was formed by the action of sulphuric acid on cellulose, but the statement is based solely on the reducing power of a complex mixture and has little significance. Schwalbe and Schultz (*Ber.*, 1910, **43**, 913) supplemented Flechsig's experiments by isolating the products of hydrolysis and obtained a semi-crystalline sugar amounting only to 20 per cent. of the theoretical yield. Working on similar lines, Ost and Wilkening (*Chem. Zeit.*, 1910, **34**, 461) made the important claim that the yield of glucose was almost quantitative, but it may be remarked that they examined the products of hydrolysis polarimetrically and reported specific rotations ranging from $+29{\cdot}4°$ to $+44{\cdot}8°$, whereas the equilibrium value for glucose is $+52{\cdot}5°$. As a further means of estimating the amount of sugar formed, they adopted methods depending on the reduction of copper solutions, but, in this case also, irregularities were experienced, and the results indicated yields of glucose varying from 73·4 to 113·5 per cent. of the weight of cellulose treated.

The use of hydrochloric acid for degrading cellulose is even less satisfactory. As is well known, Willstätter and Zechmeister (*Ber.*, 1913, **46**, 2401) dissolved cotton-wool in 40—41 per cent. aqueous hydrochloric acid, and allowed the hydrolysis to proceed in the cold. The course of the reaction was followed polarimetrically, and, by data obtained from control experiments in which glucose was dissolved in the same acid medium, they calculated that the yield of the hexose formed from cellulose amounted to 96·3 per cent. of the theoretical value. This conclusion was apparently confirmed by the results of titrations which indicated the formation of 94 per cent. of the theoretical weight of glucose. The results appear convincing until they are considered in conjunction with the known effects of hydrochloric acid upon glucose. Willstätter and Zechmeister were of the opinion that, owing to the low concentration of sugar in the acid solution, no *iso*maltose was formed, but it has been shown (Davis, *J. Soc. Dyers and Col.*, 1914, **30**, 249) that the action of hydrochloric acid in promoting the auto-condensation of glucose extends to solutions containing as little as 1 per cent. of the sugar. In addition, few reagents effect more fundamental changes in reducing hexoses than hydrochloric acid in either dilute or concentrated solution. Thus, traces of the acid convert the butylene-oxide forms of glucose into the ethylene-oxide isomerides. In higher

concentrations of acid complex changes are therefore to be expected, so that when glucose is dissolved in 44·5 per cent. hydrochloric acid the specific rotation is +164·6°, and thus exceeds the maximum value for α-glucose by approximately 50°. That Willstätter's process has very little bearing on the primary constitution of cellulose is further shown (Cunningham, T., 1918, **113**, 173) by the fact that both cotton and esparto celluloses give practically identical rotation curves when hydrolysed with concentrated hydrochloric acid under the conditions described by him. In fact, the evidence of specific rotation and reducing power, even when apparently consistent, cannot be held to characterise an uncrystallisable syrup as a definite sugar.

A considerable advance on the use of mineral acids is marked by the conversion of cellulose into glucose acetates as elaborated in the exhaustive researches of Ost and his pupils. Recognisable crystalline products consisting of cellobiose octa-acetates and glucose penta-acetates are thus obtained, so that it is possible to ascribe trustworthy values to the yields. By using acetic anhydride containing approximately 10 per cent. of sulphuric acid as the hydrolytic reagent, Ost (*Chem. Zeit.*, 1912, **36**, 1099) isolated a mixture of solid acetates amounting to 60·6 per cent. of the theoretical quantity, the remaining products being uncrystallisable syrups. It is very doubtful if the latter can be included in calculating the total yield, or if polarimetric methods are admissible in estimating hexose acetates as many factors combine to render such a method uncertain (Hudson and Parker, *J. Amer. Chem. Soc.*, 1915, **37**, 1589; Hudson, *ibid.*, 1591; Hudson and Johnson, *ibid.*, 1916, **38**, 1223).

Up to the present time, in no research on the hydrolysis of cellulose, where a yield of glucose even approximating to the theoretical amount has been claimed, have the results been based on the quantity of the sugar, or of a characteristic derivative, actually isolated. In the work now described, we adhered to the principle that the yield of hexose should be ascertained from the weight of crystalline compounds, obtained in a condition of analytical purity, and in well-defined stereochemical forms. Adopting this standard, we have been able to show that, as a minimum, the yield of glucose obtained from cellulose is 85 per cent. of the theoretical amount.

The method used by us embodies the same principle as acetolysis in that it involved hydrolysis of cellulose and simultaneous condensation of the sugar liberated, so as to give a stable derivative which thereafter remained unaffected. In this way the glucose was protected from the destructive effect of the hydrolytic agents. The material employed was a normal cotton cellulose, for a supply of which we are indebted to Mr. Wm. Rintoul, of Nobel's Explosives

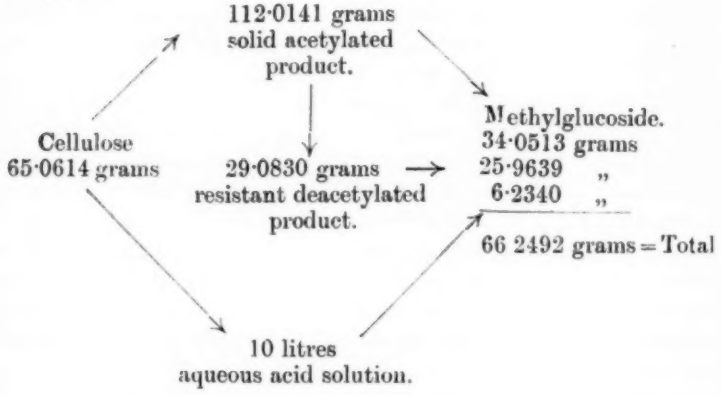
Co. This was treated, as described in the experimental part, with a large excess of acetic anhydride containing acetic and sulphuric acids. When the fibrous structure had disappeared, the product was poured into water and the precipitated solid separated. The filtrate then contained the lower acetylated glucoses, together with acetosulphates and other soluble degradation products, whilst the insoluble residue consisted of polysaccharide acetates. On heating the latter in an autoclave at 100° with methyl alcohol containing 0·5 per cent. of dry hydrogen chloride, the first effect was to remove the acetyl groups, which were converted into methyl acetate (Perkin, T., 1905, **87**, 107; Fenton and Berry, *Proc. Camb. Phil. Soc.*, 1920, **20**, 1, 16). Thereafter, simultaneous hydrolysis and condensation with the solvent ensued, the process then being parallel with the conversion of starch into methylglucoside (Fischer, *Ber.*, 1895, **28**, 1151). The main product of the reaction consisted of crystalline methylglucoside, but about 25 per cent. of the material persisted and remained practically unaffected on repeating the treatment with the acid alcohol. This amorphous residue was therefore hydrolysed by means of dilute aqueous hydrochloric acid, and the product again brought into reaction with acid methyl alcohol. In this way the total yield of methylglucoside from the fraction insoluble in water was ascertained.

Owing to the large volumes which had to be manipulated, the treatment of the products soluble in water was laborious. After removal of the free acids, the solvent was evaporated, and the sugar converted into methylglucoside in the usual way. In every case the methylglucoside was obtained as a colourless syrup which rapidly solidified to a hard mass of crystals. On hydrolysis with acid no difficulty was experienced in obtaining pure, crystalline glucose from the glucoside.

Statement of Yields Obtained.

Two methods of estimating the yields of methylglucoside were employed. The weights reported refer to pure, crystalline material dried in a vacuum oven until constant, and, as an additional check, the optical activity of each solution which yielded methylglucoside was determined. During the glucoside formation, heating with acid methyl alcohol was continued until equilibrium had been established between the α- and β-forms, and, under the conditions adopted, the proportion in which these modifications are present is respectively $\alpha = 77$, $\beta = 23$ per cent. (Jungius, *Proc. K. Akad. Wetensch. Amsterdam*, 1903, **6**, 99). The constant specific rotation attained when solutions of methylglucoside in acid methyl alcohol

are heated is thus of the order of $+114°$, so that we were able to check our gravimetric results polarimetrically. As we rely exclusively on our gravimetric data, this precaution may seem unnecessary, but its adoption secured that experimental conditions were used which precluded any possibility of the yields being affected by the formation of γ-methylglucoside. The combined results of one typical experiment are shown in the following chart, the weight of cellulose taken (70 grams) being corrected for the moisture and ash content.



Expressing the result in percentages:

Cellulose	→	Methylglucoside	→	Glucose
100 parts	gave	101·8257 parts	equivalent to	94·4775 parts.

If the cellulose molecule is composed entirely of glucose residues, 100 parts of the polysaccharide should give 111·11 parts of glucose, so that the operation of the above scheme gives a yield of methylglucoside (and therefore of glucose) of 85·03 per cent. of the theoretical amount. Although the manipulations were conducted with a standard of accuracy comparable with that employed in gravimetric analysis, it is obvious that the above result is a minimum value. The preparation of methylglucoside from glucose, although a smooth reaction, is not quantitative owing to inevitable experimental loss in isolating and crystallising the product. We do not propose, however, to introduce any correction in which allowance is made for experimental loss, and our future work will include an attempt to account for this divergence of 15 per cent. from the theoretical value.

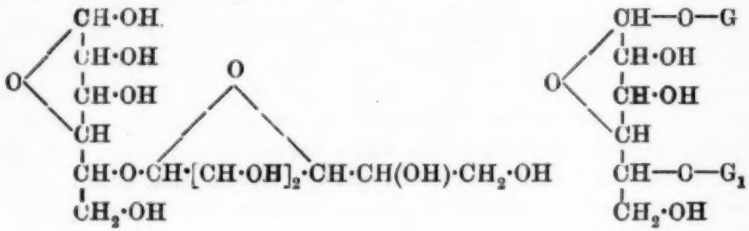
Discussion of Results.

Although the main object of the present research did not involve the detailed constitution of cellulose, some of the results obtained have a direct bearing on the problem, and may be discussed. As a rule it is an uncommon experience in the sugar group to obtain crystalline derivatives in yields which exceed 80 per cent., and the figures now submitted thus afford strong evidence that cotton cellulose is composed essentially of glucose residues condensed together. It is to be noted, however, that the processes adopted by us would not serve to isolate any ketose constituent, should such be present. In view of the fact that cellulose yields bromomethylfurfuraldehyde (Fenton and Gostling, T., 1901, **79**, 361), it is conceivable that the unexplained margin of 15 per cent. may be accounted for by the presence of a nucleus in the cellulose molecule which is resolved into a ketose on hydrolysis. It is possible, although somewhat improbable, that the hexose units in cellulose are symmetrically disposed as in inulin (Irvine and Steele, this vol., p. 1474), and the alternative has to be kept in view that two, three, or four hydroxyl groups of individual glucose molecules may be involved in the coupling. Should this be the case, the hydroxyl content of cellulose may still be regarded as three, but this would be an average value and would not imply that, as in inulin, three hydroxyl groups are present in every C_6 unit. Evidence in support of this second view has been contributed by Denham and Woodhouse (T., 1917, **111**, 244) from the study of trimethyl cellulose, and we hope, in consultation with these workers, to extend the investigation on methylated celluloses. Further evidence of the non-uniformity of the glucose linkages in cellulose is afforded by the remarkable variation in the ease with which the component parts of the molecule undergo acid hydrolysis. Another significant factor is that the yield of cellobiose obtained from cellulose, although varying greatly with the conditions of hydrolysis, has never exceeded the maximum quoted by Klein (*Zeitsch. angew. Chem.*, 1912, **25**, 1409). His figures are:

Cellulose	→	Cellobiose octa-acetate	→	Glucose
100 parts	gave	60 parts	equivalent to	31·9 parts.

From these results it would appear that at least one-third of the cellulose molecule contains the linkage characteristic of cellobiose. Now, cellobiose contains eight hydroxyl groups, one of which is a reducing group and therefore terminal. It follows that one of the remaining hydroxyl groups of the reducing component must be attached to the reducing group of the second glucose residue. The position of this linkage may be fixed from, among other factors,

the constitution assigned to trimethyl glucose, and formula I may thus be deduced for cellobiose:



(I.) (II.)

The expanded structure II, in which G and G_1 represent glucose residues, can thus be deduced for a fragment of the cellulose complex. Of the two groups, G and G_1, the latter is the more stable to hydrolysts, and the system indicated in formula II evidently represents the most resistant portion of the cellulose molecule. It is significant that in our work we encountered the same progressive difficulty in eliminating the glucose residues from cellulose. The methylglucoside obtained was isolated from three groups of acetolysis products:

A. Soluble in water.

B. Insoluble in water and hydrolysed by acid methyl alcohol.

C. Insoluble in water and resistant to acid methyl alcohol.

Our results thus show that the cellulose molecule may be dissected into three portions, and the approximate ratio in which the groups A, B, and C are present is displayed below.

		Methylglucoside.		Glucose.		$C_6H_{10}O_5$.
Cellulose 100 parts	A	gave 9·5817	equivalent to	8·9	equivalent to	8·0
	B	,, 52·3372	,,	48·6	,,	43·7
	C	,, 39·9068	,,	37·0	,,	33·3
				94·5		85·0

It will be seen that the proportion of C agrees approximately with the figure indicated by the maximum yield of cellobiose octaacetate obtained from cellulose, and it is our intention to continue the investigation by tracing the structural distinction between the units A, B, and C. In addition, we hope to ascertain whether the glucose belongs to the ethylene-oxide or butylene-oxide types, as the fundamental difference between cellulose and starch may depend on the nature of the oxidic linkage in the constituent hexose residues.

Experimental.

The material employed was a normal cotton cellulose supplied by the Research Department of Nobel's Explosives Co., Ardeer. So

far as the ultimate yields of methylglucoside are concerned, similar results were obtained with filter paper which was more readily disintegrated by the reagents. In quoting yields, allowance has been made for the moisture content (6·7 per cent.) and the ash left on ignition (0·355 per cent.).

The following is an account of a typical experiment. Seventy grams of the cellulose, cut into small pieces 2 cm. by 1 cm., were placed in an enamelled iron beaker surrounded by a bath cooled with running water. A mixture of 350 c.c. of acetic anhydride containing 6·25 per cent. of acetic acid and 20 c.c. of concentrated sulphuric acid was cooled to 15° and quickly added, the mass being rapidly agitated with a powerful stirrer. The best results were obtained when the maximum temperature did not exceed 75°, and in twenty minutes the fluid mixture was poured into ice-cold water with continuous stirring during the dilution. After twenty-four hours the white precipitate which had settled became brittle, and was filtered and washed until free from acid. The total volume of filtrate and washings was 10 litres, and the insoluble acetates, after drying at 40—50°/25 mm., weighed 112 grams. The material was separated into three portions according to the solubility in 95 per cent. alcohol: (1) soluble in the cold, (2) soluble only at the boiling point, (3) insoluble. As each fraction was convertible into methylglucoside, this separation was not carried out in the large-scale experiments.

Simultaneous Deacetylation, Hydrolysis, and Methylation of the Insoluble Acetates.

The mixed acetates were dissolved in methyl alcohol containing 0·5 per cent. of hydrogen chloride so as to give a 5 per cent. solution, and heated at 100° for seventy hours. On opening the autoclave, the odour of methyl acetate was noted, and a white, amorphous precipitate was found to have collected. This was filtered (Filtrate A), washed, and dried (Residue B).

Examination of Residue B.—The material, amounting to 29 grams, was a white, amorphous powder, insoluble in water, chloroform, ether, alcohol, or dilute hydrochloric acid, but readily soluble in dilute sodium hydroxide solution. It melted and decomposed at 237°, and reacted as a glucoside towards Fehling's solution, being hydrolysed on boiling with dilute acid. No chlorine was present, and a methoxyl determination gave a blank result (Found, C=44·0; H=6·24; OMe=0. $C_6H_{10}O_5$ requires C=44·4; H=6·20; OMe=0 per cent.).

Conversion of Residue B into Methylglucoside.

On boiling under a condenser with 3·75 per cent. aqueous hydrochloric acid, the white solid gradually dissolved with the exception of a small residue which, in a separate experiment, was hydrolysed by means of 8 per cent. acid. When the activity of the solutions was constant, indicating that hydrolysis was complete, the liquids were united, neutralised with barium carbonate, and evaporated to dryness under diminished pressure. A pale brown syrup remained, which was extracted five times with boiling methyl alcohol containing 0·5 per cent. of hydrogen chloride, and the solution was heated at 100° until the optical activity remained constant ($[\alpha]_D$ +109°, calculated on the weight of glucoside isolated). The acid was then neutralised by shaking the solution successively with lead and silver carbonates, after which the filtrate was boiled for some hours with charcoal. A colourless solution was thus obtained which, on concentration under diminished pressure, gave a clear syrup. This rapidly crystallised to a compact, hard mass on the addition of a nucleus of α-methylglucoside. The crystals were extracted five times with a large excess of boiling ethyl acetate and the pure glucoside isolated in one crop from the united liquors. The product consisted of the equilibrium mixture of α- and β-methylglucosides. Yield, 25·9 grams. (Found, C=43·20; H=7·41; OMe=15·31. Calc., C=43·30; H=7·22; OMe=15·98 per cent.)

The specific rotation in water (mean of two determinations) was +114·8°, in place of the calculated value +114·0°. The compound behaved sharply as a glucoside towards Fehling's solution, and showed the usual range of melting point (125—154°) for the mixed glucosides.

Examination of Filtrate A.—This solution contained the equilibrium mixture of α- and β-methylglucosides in acid methyl alcohol and showed $[\alpha]_D$ +113·8° (calculated on the weight of glucoside obtained). It was neutralised as described above with lead and silver carbonates, the further treatment involved in removing colloidal silver and in isolating the products being also identical. As before, no difficulty was experienced in obtaining the methylglucosides in the crystalline condition. The product was free from halogen or sulphur, and had no action on Fehling's solution until hydrolysed (m. p. 123—162°) (Found, C=43·30; H=7·15; OMe=15·56. Calc., C=43·30; H=7·22; OMe=15·98 per cent.).

The constant weight of pure glucoside was determined by heating at 50° under diminished pressure, a current of air dried over phosphoric oxide being led through the apparatus. A trap containing

the same dehydrating agent was placed between the receiver and the water-pump. Yield, 34 grams.

Preparation of Methylglucoside from Acetolysis Products Soluble in Water.

The aqueous acid filtrate obtained in removing the insoluble acetates was distinctly dextrorotatory and amounted with washings to 10 litres. This was subjected to distillation in steam, the volume being kept constant, to remove the excess of acetic acid, and the sulphuric acid present was then precipitated by shaking with barium carbonate. The filtered solution was evaporated to dryness under diminished pressure. A white, crystalline residue remained, together with a yellow syrup which was extracted five times with boiling methyl alcohol containing 0·5 per cent. of hydrogen chloride, the extraction process extending over ten hours. The united extracts (Solution C) were separated from the semi-crystalline, undissolved solid (Residue D).

Examination of Residue D.—Although largely inorganic, this residue contained some organic matter, derived either from soluble acetosulphates or from colloidal cellulose acetates. It was accordingly treated in exactly the same manner as Residue B and the hydrolysis product isolated as a syrup. This was extracted six times with boiling methyl alcohol containing 0·5 per cent. of hydrogen chloride and the solutions were united with Solution C.

Examination of Solution C.—This extract, together with that from Residue D, was heated at 100° until the rotation became constant, after which the equilibrium mixture of the methylglucosides was isolated in the usual manner. Somewhat greater difficulty was experienced in obtaining the product in a pure condition, and although the material behaved sharply as a glucoside towards Fehling's solution, the melting point showed a wider range than usual (105—140°). The specific rotation was also slightly low ($[\alpha]_D$ +111·5° in place of +114°). Yield, 6·2 grams (Found, C=43·17; H=7·16; OMe=15·22. Calc., C=43·30; H=7·22; OMe=15·98 per cent.).

Isolation of Crystalline Glucose from Cellulose.

The preparations of crystalline methylglucoside, obtained as described, were mixtures of the α- and β-forms in equilibrium. This was confirmed by crystallising a sample slowly from methyl alcohol. The β-form was then retained in solution, and the α-iso-

meride which separated, showed, after drying at 50°/25 mm., $[\alpha]_D$ +157·5° in water. This agrees exactly with the standard value (+157·6°). Moreover, the material melted at 165°, the melting point being unaffected by admixture with pure α-methylglucoside.

Further proof of the standard of purity attained was afforded by the hydrolysis of the mixed glucosides. A 5 per cent. solution in 4 per cent. hydrochloric acid was heated at 100°, polarimetric readings being taken every fifteen minutes. The permanent value observed, when calculated for the weight of glucose formed, was +53·0° in place of +52·5°. After neutralisation with barium carbonate and evaporation to dryness under diminished pressure, a syrup mixed with barium chloride remained. This was extracted with boiling absolute alcohol, the solution decolorised, filtered, and slowly concentrated at a low temperature. On nucleation and stirring, crystalline glucose readily separated. After a second crystallisation from absolute alcohol, the yield of dry sugar amounted to 60 per cent. of that required by theory. The glucose melted at 145° and gave glucosephenylosazone (m. p. 204—205° uncorr.) (Found, C=39·97; H=6·54; OMe=0. Calc., C=40·00; H=6·67; OMe=0 per cent.).

When dissolved in water the initial specific rotation of +100·8° was recorded, and this diminished to the constant value of +52·37°. The above result proves conclusively that the methylglucoside employed did not contain any isomeric methylhexoside, and that consequently no mannose or galactose residues are present in cellulose.

We desire to record our thanks to the Royal Commissioners for the 1851 Exhibition for a Research Scholarship held by one of us during the progress of the above research.

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CLXVI.—*The Influence of Lead on the Catalytic Activity of Platinum.*

By Edward Bradford Maxted.

In a recent investigation (T., 1919, **115**, 1050; this vol., p. 1280) dealing with the inhibitive effect of hydrogen sulphide on the occlusive power of palladium for hydrogen, it has been found that a linear relationship exists between the mass of poison absorbed by the palladium and the resulting depression in its occlusive power for hydrogen. In view of the intimate connexion which undoubtedly exists between the occlusive power of a preparation for hydrogen and its activity for catalytic hydrogenation, work has now been undertaken with the object of following quantitatively the influence of the addition of successive small increments of a catalyst poison on the subsequent activity of a catalyst for catalytic hydrogenation.

In the measurements described in the present paper, lead has been chosen as a typical non-volatile catalyst poison, finely divided platinum being employed as a catalyst. From the results obtained, the catalytic activity of platinum would appear to be a linear function of the lead present, this relationship being analogous to that obtained for the influence of a poison on the occlusive power.

Experimental.

The method adopted consisted in measuring the velocity of absorption of hydrogen by a given weight of oleic acid, under standard conditions, in the presence of a fixed amount of finely divided platinum, to which was added a variable proportion of a lead salt. The shaker and measuring apparatus employed were similar to that previously used for measurements of the velocity of hydrogenation in the presence of varying amounts of carbon monoxide (*Trans. Faraday Soc.*, 1917, **13**, 36). In order to avoid the presence of more than one liquid phase, both the oleic acid and the lead salt were dissolved in glacial acetic acid, the lead being employed in the form of acetate.

For the preparation of a platinum catalyst of approximately uniform activity, a weighed quantity of hydrated platinic oxide was suspended in stearic acid and reduced in this medium by means of pure hydrogen. The suspension was agitated during cooling in order to obtain a solid product containing an approximately uniform concentration of platinum. Each gram of this stock

catalyst was found, on analysis, to contain 0·0634 gram of platinum, 0·1653 gram of the catalyst, corresponding with 0·0105 gram of platinum, being taken for each experiment.

For the standard solution of lead acetate, 0·2 gram of pure lead, prepared by the electrolysis of lead borofluoride (*Zeitsch. anorg. Chem.*, 1910, **67**, 339), was dissolved in nitric acid and converted into oxide by ignition. The lead oxide was subsequently dissolved in glacial acetic acid, in which, however, lead acetate is only sparingly soluble, and was made up to 1 litre with the same solvent. Careful analysis of the filtered liquid showed that each c.c. of the solution contained 0·00017 gram of lead.

In order to ensure uniformity, the oleic acid and glacial acetic acid employed were each taken from a stock bottle containing sufficient for the whole of the measurements. For convenience in working, both acetic and oleic acid were measured by volume, by means of a graduated pipette, 3 c.c. of the latter being in each case dissolved in sufficient acetic acid to total, with the acetic acid subsequently added with the lead, 9 c.c. of acetic acid in all.

The hydrogenation reaction was carried out in a thermostat at 50°, the desired quantity of standard lead acetate solution being previously added to the reaction mixture, which was allowed to remain in the thermostat for about half an hour before starting the shaker.

Table I summarises the results of a series of experiments carried out under the above conditions.

TABLE I.

C.c. of standard lead solution added.	Ratio gram-atoms Pb to gram-atoms Pt.	Hydrogen absorption in c.c. after					
		1 min.	2 mins.	4 mins.	6 mins.	8 mins.	10 mins.
0·0	0·0	10·9	21·6	40·8	58·4	74·1	88·6
0·0	0·0	11·0	20·8	38·5	54·2	67·5	82·8
0·5	0·0076	9·4	17·2	30·8	42·6	52·0	58·9
1·5	0·023	7·5	14·0	25·5	35·4	43·5	49·0
2·5	0·038	7·0	13·0	23·0	31·0	37·6	42·8
3·0	0·046	6·6	12·2	21·6	29·8	36·5	42·1
4·0	0·061	5·0	9·9	17·0	22·3	26·4	29·4
5·0	0·076	2·9	5·4	9·4	12·6	15·2	16·9
5·0	0·076	2·8	4·9	8·2	10·9	12·8	14·3
6·0	0·916	2·2	4·2	7·3	9·5	10·6	11·4
7·0	0·107	nil	—	—	—	—	nil
7·5	0·114	nil	—	—	—	—	nil

It would appear to be justifiable to take as a measure of the activity of a given catalyst the intensity of the effect produced by it, this effect being, in the present instance, the velocity of the absorption of hydrogen induced by a given weight of platinum under standard conditions. Since, however, this velocity changes

as saturation proceeds, it becomes necessary to choose an equivalent point on the absorption curve at which the velocity induced by the various catalysts becomes comparable. Armstrong and Hilditch (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 137, 322) have shown that, with pure substances, the velocity of absorption, in place of following the unimolecular formula, as was formerly supposed, does not change appreciably as hydrogenation proceeds until a certain point of inflexion is reached, when it rapidly decreases. These authors consider that the regular curves, usually obtained with materials of ordinary purity, are due to the presence of impurities, possibly in the present case to "clogging" poisons of an albuminoid nature. It is not proposed in the present paper to discuss further this most interesting point, and, for the sake of simplicity, the progress of the absorption with the time may be expressed in a form independent of any general theory, by an expression of the conventional algebraic type, $V = at + bt^2 + ct^3$, in which a, b, and c are constants and V is the volume in c.c. of hydrogen absorbed after t minutes. From the absorption curve, expressed in this form, the initial velocity of absorption induced by the platinum may readily be obtained by differentiation. This initial induced velocity represents the rate at which hydrogen would continue to be absorbed in the presence of the given catalyst if no disturbing factors, due either to the presence of impurities or to the nature of the reaction, were present, and affords a simple means of expressing numerically the activity of the catalyst promoting the reaction.

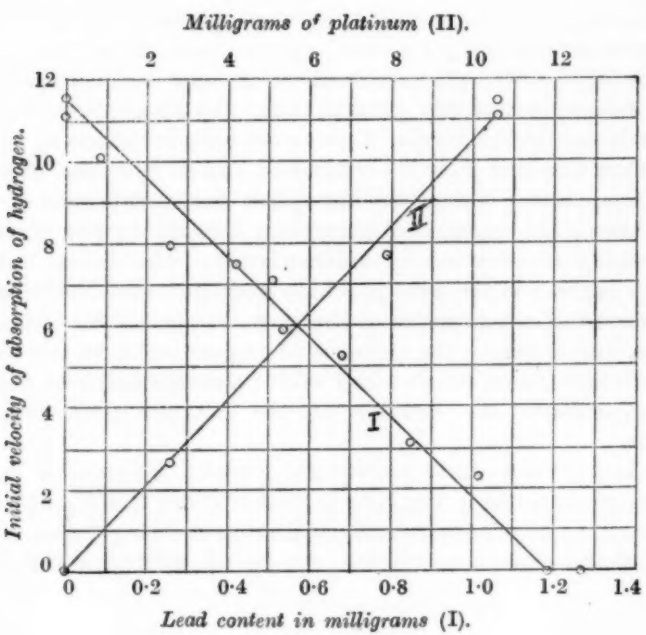
In table II, the curves corresponding with the figures of table I have been expressed in the form indicated above, the absorption at one minute, four minutes, and ten minutes being taken as the basis of the expressions, which correspond well with the entire curve.

TABLE II.

C.c. of lead solution added.	Values of		
	a.	*b*.	*c*.
0·0	11·14	−0·238	0·0011
0·0	11·56	−0·588	0·0260
0·5	10·1	−0·714	0·0295
1·5	7·94	−0·447	0·0144
2·5	7·49	−0·511	0·0191
3·0	7·10	−0·512	0·0224
4·0	5·26	−0·267	0·0035
5·0	3·12	−0·224	0·0082
5·0	3·11	−0·332	0·0163
6·0	2·33	−0·131	0·0012
7·0	0·0	—	—
7·5	0·0	—	—

On differentiating these equations in order to obtain the initial induced velocity, the interesting result is obtained that the depression of the catalytic activity of the platinum, due to the presence of increasing proportions of lead, follows a linear law analogous to that observed for the inhibition of occlusion. This point is strikingly illustrated in graph (1) of the figure, in which catalytic activity, measured by the initial induced velocity of reaction, has been plotted against the lead content of the system.

The constants b and c of table II, representing the decrease in the velocity of absorption with the time, do not change regularly



with increasing lead content, but vary somewhat widely from experiment to experiment round a mean value, the deviation from this mean being probably caused by the difficulty in producing exactly corresponding conditions of experiment, and being observed also during a number of measurements carried out with platinum alone in the absence of a poison.

It would appear that the action of lead is to inhibit completely the catalytic activity of a certain proportion of the catalyst, each milligram of lead rendering inactive about 8·8 milligrams of platinum, whilst the residual platinum remains capable of functioning normally. This conclusion was further strengthened by

experiment 3 of table I, which, although included in the general results, was carried out under somewhat different conditions from the other measurements. In this case, whilst the weight of oleic acid and acetic acid remained that usually taken, the platinum catalyst corresponded with 50 per cent. more platinum than that normally employed, namely, to 0·0157 gram in place of 0·0105 gram. To this, 4 c.c. of the standard lead solution were added. If the conclusion just stated is correct, the result should be equivalent to a normal experiment with 0·0105 gram of platinum, in which 0·5 c.c. of lead solution has been added. That this is the case is well shown by the manner in which the initial absorption corresponds with the poisoning line at the point required by 0·5 c.c. of lead solution, and the measurement has therefore, for the sake of brevity, been included in table I under this heading.

The view that a certain proportion of the catalyst is poisoned by each milligram of lead added, the remaining catalyst functioning normally, involves the tacit assumption that the initial velocity of absorption, induced by varying weights of catalyst under otherwise identical conditions, varies directly with the weight of platinum available for hydrogenation. That this is actually the case was shown by means of a series of experiments with platinum alone, in which the weight of this metal was reduced to three-quarters, one-half, and one-quarter of that taken for the experiments of table I. The results obtained are summarised in table III.

TABLE III.

Wt. of Pt in milligrams.	Hydrogen absorption in c.c. after					
	1 min.	2 mins.	4 mins.	6 mins.	8 mins.	10 mins.
10·5	10·9	21·6	40·8	58·4	74·1	88·6
10·5	11·0	20·8	38·5	54·2	69·5	82·8
7·9	7·4	14·3	26·6	37·2	46·4	53·6
5·2	5·5	10·4	17·3	22·5	26·6	29·1
2·6	2·3	4·2	6·8	9·0	10·5	11·3

Table IV contains the coefficients a, b, and c of the absorption curves corresponding with the figures of table III, expressed in the conventional algebraic form previously employed, and in graph (II) of the figure the initial velocity of absorption, obtained, as before, from these curves by differentiation, has been plotted against the weight of platinum taken, the linear relationship between these quantities being clearly marked. The conditions, other than the constancy of the weight of platinum taken and the absence of lead, were similar to those employed above.

TABLE IV.

Wt. of Pt in milligrams.	Value of		
	a.	*b.*	*c.*
10·5	11·14	−0·238	0·0011
10·5	11·56	−0·588	0·0260
7·9	7·66	−0·270	0·0040
5·2	5·96	−0·478	0·0173
2·6	2·66	−0·381	0·0228

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CLXVII.—*The Investigation of Sodium Oleate Solutions in the Three Physical States of Curd, Gel, and Sol.*

By MARY EVELYN LAING and JAMES WILLIAM McBAIN.

ONE of us (M.E.L.), in continuing previous work (T., 1919, **115**, 1280), has now found that aqueous sodium oleate at temperatures between 0° and 25° can be brought at will into any one of three typical states, namely, clear oily liquid sol, clear transparent elastic gel, or white opaque solid curd, all at one and the same concentration and temperature.

Hitherto, the last two types have not been differentiated, although, as will be shown, they are wholly independent and exhibit very different properties. Probably nearly all of the observations on solidified soap systems recorded in the literature refer to what we have here defined as soap curd, and some confusion would have been avoided if the existence of these two separate types had been recognised (see, for example, the controversy between Zsigmondy, Bachmann, and von Weimarn with regard to whether or not soaps are "gels"). The real soap gels are unmistakable, since they resemble gels of gelatin. It has become evident that, under suitable conditions, all soaps may exist in these three forms, and each form is important both for the theory and manufacture of soaps.

The chief experimental discovery described in this paper is that soap sol and soap gel are identical in all respects, with the exception of elasticity and rigidity, which are characteristic of the gel form alone. The following properties are all identical in sol and

gel: (i) electrical conductivity;* (ii) lowering of vapour pressure, which measures the amount of substance in true solution; (iii) refractive index; and (iv) as Salmon has recently shown in this laboratory (this vol., p. 536), the concentration of the sodium ion.

A soap curd, on the contrary, is a sol or gel from which a part or nearly all of the soap has been abstracted through the formation of white curd fibres, as Darke, McBain, and Salmon have shown in another communication. The distinctive structural feature of soap curd is the separation of hydrated soap as a felt of long, white fibres, these fibres being of barely microscopic diameter. Zsigmondy maintained that the formation of the soap curds which he studied was essentially a process of crystallisation; the analogy is certainly close.

It would seem an unavoidable conclusion from the observed identity of so many properties of the sol and gel of soap that the chemical equilibria are the same, and that therefore the colloidal particles present in the two are identical both in nature and amount. It is evident that this is of direct significance in the general theory of the structure of gels.

It has long been known that salt solutions retain the greater part of their conductivity and diffusibility when gelatinised by the addition of gelatin. This was, however, less surprising, since the conductivity could be largely ascribed to the electrolyte, and to this extent it was a matter of indifference what happened to the gelatin on gelatinisation. To those who regarded the gelatin solution as heterogeneous, whether in the form of sol or gel, any alteration in the degree of dispersion, even amounting to removal of the gelatin from solution, need not necessitate any great change in the conductivity of the dissolved salt.

No such explanation is possible in the case of soap solutions where no extraneous chemical is present, and where the colloid arises from, and is in true equilibrium with, the crystalloidal constituents. Any essential alteration in amount or degree of dispersion of the soap colloid would have been instantly reflected in changed conductivity, well illustrated in the behaviour of curds.

A further point to be mentioned here is that the gel, in its genesis, is much more closely related to the curd than to the sol. With the less concentrated solutions, it was found almost impossible

* Since this paper was submitted for publication, it has been pointed out to us that Arrhenius so long ago as 1887 (*Oefvers. Stockholm Akad.*, **6**, 121) showed that the conductivity of gelatin–water–salt systems is the same whether in the sol or gel condition. This was quite unknown to us and, so far as we know, this important observation has been overlooked.

to prepare a gel except through formation of a curd, which was then gently warmed until it became clear. On careful cooling, it could be retained in the form of gel. This is at complete variance with the emulsion conception of gelatinisation as involving merely a large increase in viscosity on lowering through a small zone of temperature.

It would seem necessary throughout the discussion of colloids to distinguish clearly between gelatinisation and coagulation, that is, between the formation of a gel and a curd or coagulum, whether the latter is irreversible, as in the case of a boiled egg, or reversible, as in the case of a soap curd.

The experimental data here presented include, first, systematic measurements of the conductivity of sol, gel, and curd of sodium oleate over the whole range of temperature, 0—28°, at which it is possible to obtain gel or curd. These are supplemented by measurements of refractive index and of vapour tension, and by direct analyses. Finally, some observations on the behaviour of curds of mixtures of soaps are recorded.

Experimental.

The earlier experiments had to be carried out with a Kohlrausch (Köhler) apparatus, whereas with the final work a set of Washburn (Leeds and Northrup) apparatus was available.

Even when not using the pure sine wave current from the Siemens high-frequency machine or the Vreeland oscillator, but with an ordinary induction coil, the position of the minimum was defined with an eight-fold accuracy by the Washburn set as compared with the Köhler apparatus. This is important, for it means that even small differences in conductivity between gel and sol, had they existed, would have been measurable on such a bridge, even if they would not have been detected on the ordinary metre wire.

All resistances, bridge wires, thermometers, etc., were carefully calibrated. The thermostat temperatures were constant within 0·01°. The special conductivity cells of borosilicate glass have already been described (see McBain, Laing, and Titley, T., 1919, **115**, 1279). The cell constants at 0° were 13·06 and 0·1664, and at 20° 13·20 and 0·1690 (compare McBain and Coleman, *Trans. Faraday Soc.*, 1917, **15**, 36, who obtained a similar variation with temperature when using Kohlrausch's standard values).

Preparation of the Soaps.

Apart from more than a year's delay in securing the necessary oleic acid, there was unexpected difficulty owing to the lack of

purity of the materials ultimately obtained. Pending the routine tests, soaps were prepared immediately on the arrival of various specimens which had proved satisfactory in pre-war work. Table I contains some of the iodine values and molecular weights as obtained by titration of specimens supposed to be pure. Specimens marked "K" were palmitic and oleic acid "Kahlbaum." The iodine value was determined by the Wijs method, for which pure palmitic and oleic acids should give the values 0 and 90 respectively.

TABLE I.

Tests of Fatty Acids.

Specimen.	Iodine value.	Mol. wt. Titration.	Mol. wt. Theory.
Palmitic "K" pre-war	1·0	256·1	256·1
Palmitic "K" post-war	3·0	256·9	256·1
British post-war	10·0	262·8	256·1
Oleic "K" pre-war bottled	66·6	299·5	282·2
Oleic "K" pre-war sealed.....	90·14	—	282·2
Oleic "K" post-war sealed	90·14	285·5	282·2
British post-war sealed	88·9	286·5	282·2

The soap solutions were prepared from oleic acid and sodium drippings free from carbon dioxide in stoppered bottles of Jena glass in the manner previously described. The hydroxide was standardised against hydrochloric acid (method of Hulett and Bonner, *J. Amer. Chem. Soc.*, 1907, **31**, 390), as well as against pure oxalic acid. Concentrations are invariably expressed in weight-normality, gram-molecules per 1000 grams of water.

In all, four series of measurements were carried out with sodium oleate. In series *A*, solutions of good sodium oleate were employed, although they had been kept since the previous communication (T., 1919, **115**, 1279). Although the actual data are not here recorded, they in themselves sufficed to establish the main conclusions, now confirmed and extended.

Series *B* was carried out using the oleic acid of the fourth horizontal row of table I. Evidently it had become partly oxidised by exposure to air, as shown by the iodine and titration values. Here again sol and gel are identical, and the values for curd are of interest as showing the high conductivity of a curd which was not more than a few hours old.

Series *C*, made with the oleic acid of the sixth horizontal row in table I, contained 1·5 per cent. excess of alkali. All the data obtained in this, the principal, series have been corrected by the 3·8 per cent. predicted from the measurements of McBain and Taylor (*Zeitsch. physikal. Chem.*, 1911, **76**, 178), and it will be

noted that they agree within a fraction of 1 per cent. with the three measurements already published.

Series *D* was carried out with the same specimen of oleic acid, using neutral solutions prepared by taking the experimentally determined quantities of acid required, as recorded in table I.

Density Measurements.

The density was found for each concentration at these low temperatures with a 10 c.c. pyknometer. The densities found give straight-line graphs when plotted against concentration, the values, except for 0·2*N* above 18°, being only slightly greater than unity.

TABLE II.

Densities of Sodium Oleate Solutions.

	Concentration.		
Temperature.	0·2N_w.	0·4N_w.	0·4N_w:
0°	1·0012	1·0040	1·0068
10	1·0005	1·0029	1·0062
18	0·9997	1·0020	1·0050

(Values above 18° extrapolated.)

Method of obtaining the Curd or Gel.

There are definite temperature limits to the existence of each of the states gel and curd. Thus a 0·4*N*-gel could not be obtained at 0° or the 0·4*N*-curd above 23°; 0·6*N*-gel and sol were not obtained below 6°, or the 0·6*N*-curd above 25°. Both 0·4*N*- and 0·6*N*-gel rapidly liquefied at 25°.

The gel was obtained in almost every case by very slow warming of the curd, which gradually lost its opacity, first becoming cloudy and then turning to a clear gel of definite shape. In the case of 0·2*N*- and 0·4*N*-soap, the gel was always surrounded by a film of sol at least 2 mm. thick in the centre of the cell and for 4—6 mm. above each electrode. The gel column is firmly attached to each electrode, and the sol surrounds it. With rising temperature, the gel shrinks more and more, remaining attached to the electrodes at each end, until there is only a fine, diaphanous thread connecting the two small masses of gel.

The 0·6*N*-solution was always obtained as either sol or gel, not having a boundary line, as in the other cases mentioned. With this concentration alone, a gel was obtained by cooling the sol. With slow cooling, the whole viscous sol set to a gel, which curded very gradually (that is, after two days). The curd formed in each limb spread towards the centre in long, silky fibres, which gradually

became more and more opaque, until the whole mass was white curd with individual fibres no longer distinguishable.

The 0·2*N*- and 0·4*N*-sols, when cooled, developed large, white nuclei in isolated spots, and these nuclei grew towards each other by thickening filaments. Thus a clear gel was not obtained in these cases from the cooling side. Whenever the nuclei appeared, the conductivity always dropped appreciably, but when, as in the case of 0·6*N*-gel, the fine fibres appeared, it was not until the whole was cloudy that the lowering of conductivity became appreciable. When the nuclei formed, the soap was evidently being removed from the sol in considerable quantities, whereas for a few

The Conductivity Data.

TABLE III.

Molecular Conductivity of Sodium Oleate.

(Series *B*, alkaline, see p. 1509.)

Temperature.	0·2*N*.			0·4*N*.		
	Sol.	Gel.	Curd.	Sol.	Gel.	Curd.*
0·0°	13·42	13·38	5·88	14·16	—	7·19
5·5	14·63	14·82	6·97	16·77	16·78	8·97
11·0	17·54	17·33	9·55	19·70	20·04	10·43
15·0	21·25	21·25	—	24·48	24·43	21·32
20·0	—	—	—	26·02	26·04	—
22·0	—	—	—	27·00	27·00	—

* Fresh curd not more than a few hours old in each case; often a day elapsed between measurement of gel and sol at any one temperature, but the order in which these were measured did not affect the result.

TABLE IV.

Molecular Conductivity of Sodium Oleate Solutions.

(Series *C*, corrected for alkalinity.)

Temperature.	0·4N_w.			0·6N_w.		
	Sol.	Gel.	Curd.*	Sol.	Gel.	Curd.*
0·0°	—	—	3·253	—	—	2·547
5·0	13·94	13·94	4·248	15·10	—	3·046
10·0	16·22	16·22	6·015	16·95	16·94	4·341
15·0	19·13	19·13	—	20·37	20·33	6·393
18·0	20·95	20·94	—	21·65	21·65	12·96
22·0	22·62	22·62	—	22·64	22·64	—
25·0	25·87	25·81	—	25·97	25·97	—

* The curds were kept four days at 0°, and during two subsequent days were gradually warmed to the ordinary temperature. The temperature was kept constant at each intermediate temperature before the conductivity was noted. Sometimes a week elapsed between the measurements of gel and sol, without affecting the constant value obtained before and after such treatment.

TABLE V.

Comparison of Specific Conductivities of Curds and Gels.

(Series *C*.)

Temperature.	Curds.		Gel (or sol.).	
	0·4*N*.	0·6*N*.	0·4*N*.	0·6*N*.
0°	0·01168	0·001304	—	—
5	0·001 19	0·001555	0·004983	0·007729
10	0·002150	0·002213	0·005805	0·008632
15	0·003169	0·003255	0·006821	0·01038
18	0·004529	0·006594	0·007494	0·01101
20	0·005597	—	0·008065	0·01161
25	—	—	0·009196	0·01320

TABLE VI.

Specific and Molecular Conductivity of Curds of Sodium Oleate at 0°.

(Series *D*, neutral.)

Days.	0·2*N*.		0·4*N*.		0·6*N*	
	k.	*μ*.	*k*.	*μ*.	*k*.	*μ*.
1	0·0009661	4·860	0·001171	3·268	0·001162	2·273
2	0·0008908	4·478	0·001137	3·176	0·001140	2·229
3	0·0008672	4·362	0·001114	3·111	0·001135	2·219
7	0·0008339	4·195	0·001072	2·994	0·001126	2·203
14	0·0008106	4·078	0·001014	2·832	0·001114	2·178
21	0·0008066	4·057	0·0009858	2·754	0·001112	2·174
28	0·0008028	4·038	0·0009734	2·719	—	—
40	0 0008138	(4·094)	0·0009580	2·676	—	—
56	—	—	0·0009417	2·630	—	—
65	—	—	0·0009328	2·609	—	—

TABLE VII.

Specific and Molecular Conductivity of Aged Curds of Sodium Oleate from* 0° *to* 20°

(Series *D*, neutral.)

Temperature.	0·2*N*.		0·4*N*.		0·6*N*.	
	k.	*μ*.	*k*.	*μ*.	*k*.	*μ*.
0°	0·0008028	4·038	0·009328	2·609	0·001112	2·174
5	0·0009666	4·867	0·001160	3·243	0·001277	2·479
10	0·001190	5·994	0·00170	4·752	0·00179	3·506
15	0·001930	9·735	0·00282	7·893	0·003146	6·167
18	0·002720	13·71	0·00414	11·32	0·004700	9·217
20	0·003572	18·01	0·005501	15·40	0·006577	12·90

* The curds in the thermostat, after completion of table VI at 0°, were allowed to attain the ordinary temperature while these measurements were being taken ; this occupied four more days.

Figures 1 and 2 present the conductivity data and show at a glance the effect of time, of temperature, and of concentration, besides showing the relative magnitudes of the specific conductivities of sols, gels, and of aged curds.

faint fibres only very small amounts were being removed. In every case where the gel exhibited a conductivity slightly less than that of the sol, this could be directly traced to the presence of a few curd fibres.

The sol was always obtained by warming the gel or curd to 20° or 30°.

Analysis, Refractive Index, and Vapour Pressure of Sols and Gels.

It was first established that the refractive index of 0·5*N*-sodium oleate as gel is identical to eight significant figures with that of the same solution as sol. A Zeiss interferometer with 3-cm. cell was employed. Into one side was placed some of the sol, and, after it had been caused to gelatinise, more of the same sol was poured into the other side for direct comparison, without causing alteration of more than one division from the position of the zero reading, corresponding with a difference in concentration of $10^{-6}N$. This confirms the result of the conductivity measurements, and also of Salmon's measurements of sodion concentration, using the sodium electrode (*loc. cit.*). A similar result has been obtained for gel and sol of gelatin by Walpole.

The identity in properties of sol and gel is shown also by the following measurements of vapour tension,* using the dew-point method of McBain and Salmon (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 44; *J. Amer. Chem. Soc.*, 1920, **42**, 426).

Dew-point Lowering of Sodium Oleate at 18°.

Concentration.	Gel.	Sol.
0·6*N*	0·06°	0·06°
0·4*N*	0·04	0·04

Experiments were next carried out to test whether appreciable segregation of soap occurs during gelatinisation.

A 0·4*N*-curd was introduced into a clean, dry test-tube and very gently warmed. The curd very gradually became a column of gel with sol surrounding it. After some time, the contents were poured through silver gauze into a dry, weighed flask, the sol passing through, the gel remaining on the gauze. Some of this gel was removed into a second tared vessel, and both weighed specimens were carefully tested, both for sodium and for oleic acid (or oleate), by titration with about $N/4$-solutions of aqueous and

* Vapour pressure is used as a measure of the concentration of crystalloidal constituents present; the vapour pressure of gels and sols containing no crystalloidal material does not possess any such significance, since it is necessarily the same as that of the solvent itself.

alcoholic sodium hydroxide standardised against the oleic acid used (molecular weight 286·5, instead of the theoretical 282·2). Two such experiments are recorded below, the sodium and oleic acid content being expressed in c.c. of 0·2*N*-acid.

	Weight taken.	Type.	Sodium.	Oleic acid.	Soap calculated per 100 grams.	Difference sol/gel per cent.
1.	6·2272	gel	10·55	10·48	33·8	0·9
	5·4344	sol	9·43	9·42	34·7	
2.	2·2807	gel	3·94	3·93	34·53	0·08
	4·0814	sol	7·11	7·00	34·56	

It is evident from the above table that the sol and gel have nearly the same composition. Even after allowing considerable time for shrinking and possible syneresis, the result expected would be similar to the above, since the conductivity of an old gel is the same as that of freshly formed gel and as that of the sol into which it turns.

A similar experiment was made with 0·5*N*-sodium oleate, using the Zeiss interferometer with 5 cm. cell. The difference in concentration between lumps of gel and the sol in which they were floating was not more than 0·003*N*. Perhaps even this small difference may have been due to segregation caused by previous curding, which could not be equalised again without melting the gel for the purpose. From all the above, it is evident that, in complete contrast to formation of curd, formation of gel takes place without appreciable segregation of the soap. The refractive index of a soap solution is an accurate measure of the total concentration of soap, whether as sol or gel.

Discussion.

Theory of Gels.

It would appear from the present work that a gel is identical with a sol except for its mechanical properties.* Osmotic activity, electromotive force, and conductivity alike prove that the chemical equilibria are identical in gel and sol. Furthermore, since the conductivity of concentrated gel and sol is thus identical, the hypothesis of a closed cellular, spongy, or honeycomb structure or other similar structure is disproved, and even a similar structure with partly open pores is rendered extremely unlikely [see (1) and (2) below].

* Previous communications have indicated that soaps are to be classed with proteins, gelatin salts, dyes, etc., as colloidal electrolytes. The similarity in the behaviour of their sols is so definite that any general theory must be consistent with the facts of all these cases. Hence the significance of the identity of soap sol and gel must extend to these other systems.

A difficulty in reviewing the various opinions held with regard to the structure of gels is that a definition of the word phase is primarily involved. The old diversity still subsists as to whether typical colloidal sols and gels are to be called one-phase or two-phase systems. Thus, whereas most authors are agreed that sols and gels are to be regarded as heterogeneous systems, a few, such as Proctor, Hayes, and Brailsford Robertson, prefer to call them one-phase systems, even where they postulate a molecular network throughout the gel. It was arguable to regard sols and gels of protein salts as one-phase systems containing only molecularly dispersed matter until the facts with regard to soap sols and gels had been established. In the case of soap solutions, the formula and molecular weight of the chemical substance concerned are known, and it is impossible to ascribe the colloidal properties to the presence of unknown molecules of enormous molecular weight. So long as the soap is in molecular dispersion, it behaves as an ordinary crystalloid.

Apart from the above conception of a molecular network, there are four suggestions which have been advanced to account for the properties of gels, namely:

(1) Closed honeycomb solid–liquid; Freundlich.

(2) The porous, but continuous, solid cellular framework; Hardy and Lloyd.

(3) The emulsion, liquid–liquid; Wo. Ostwald.

(4) The micellar theory of Nägeli, Pauli, Zsigmondy, and the present authors.

Various authors, whilst adhering to one or other of the above conceptions, have argued that the phenomenon of gelatinisation is a process of crystallisation. The evidence here presented is, however, incompatible with this suggestion if crystallisation is taken to be removal of substance from the colloidal solution (see, for instance, Levites, 1908; Zsigmondy and Bachmann, 1912, etc.; Bradford, *Biochem. J.*, 1918, **12**, 351; 1920, **14**, 91; Bogue, 1920; Lloyd, *Biochem. J.*, 1920, **14**, 147). Thus coagulation and formation of curd are differentiated from gelatinisation. The present data give but little information with regard to the question as to whether the individual colloidal particles of soap gels and sols are to be regarded as "crystalline" or amorphous, but the fact remains that in the process of gelatinisation they are not sufficiently removed from solution to disturb the equilibria into which they enter. Since they are identical in sol and gel, and since they exhibit properties of aggregation or orientation, it is more difficult to conceive of them as liquids. These terms, however, lose much of their meaning when applied to particles of ultramicroscopic and

amicroscopic dimensions such as exist in these typical "emulsoid" systems.

As a result of the optical observations of Bütschli (1892—1900) and of Hardy (1899) and Quincke, an emulsion theory of gels, whether (1) or (2) or (3) above, was regarded as finally established (see, for instance, Freundlich, "Kapillarchemie," 1909, p. 475). Most authors considered that the emulsion had solidified to a cellular or honeycomb structure, a conception which is irreconcilable with the definite experimental evidence here presented. Wo. Ostwald (1905) regarded the emulsion as still consisting of two liquids, and several authors have suggested that gelatinisation consisted of the inversion of these two liquids, the dispersed phase becoming, in its turn, the dispersion medium. This, again, is clearly contradicted by the experimental data for soap gels, since gelatinisation leaves conductivity quite unaffected. Further, Hatschek (*Trans. Faraday Soc.*, 1916, **12**, 17) showed that the viscosity of a gel does not exhibit the behaviour characteristic of an emulsion of two liquids.

The very earliest explanation of gels was the micellar theory of Frankenheim (1835) and Nägeli (1858). They considered that gels owe their characteristic properties to a loose network or aggregation of ultramicroscopic or amicroscopic solid particles. Zsigmondy and Bachmann resuscitated this theory, producing strong experimental evidence in its favour, as was pointed out by Pauli at the time.

They showed that the heterogeneity of gels is of a different order of magnitude from that assumed by Bütschli, Hardy, etc., whose observations were made before the invention of the ultramicroscope. The heterogeneity is amicroscopic instead of microscopic, involving distances of less than one hundredth of a micron. They emphasised the very important point that in all the positive experiments of Bütschli and of Hardy some procedure was adopted, or chemical added, to produce the structure observed in the microscope, as had, indeed, been pointed out by Pauli in 1902.

The micellar theory is in harmony with the phenomena of syneresis, double refraction, swelling, peptisation, the definite form and elasticity of gels, coagulation, dehydration and vapour-pressure curves, pleocroism, optical and ultramicroscopic phenomena, the behaviour of protected colloids, such as gold particles, which retain their identity even after repeated transformations, such as gelatinisation, in other words, all the characteristic properties of gels. All that is necessary is to assume that the particles become stuck together or oriented into loose aggregates, which may be chance granules or, more probably, threads. This hypothesis is

supported by many other phenomena, such as those observed by Garrett (*Phil. Mag.*, 1903, [vi], **6**, 374), Shreve (*Science*, 1918, **48**, 324), Holmes, Kaufmann, and Nicholas (*J. Amer. Chem. Soc.*, 1919, **41**, 1329), Shoji (*Biochem. J.*, 1919, **13**, 227), Lloyd (*ibid.*, 1920, **14**, 147), Bogue (*Chem. Met. Eng.*, 1920, **23**, 62), and Lifschitz and Brandt (*Kolloid Zeitsch.*, 1918, **22**, 133).

The conception of micellar orientation to which the present evidence so directly leads is supported by many other facts, such as the following. Thus, on heating a gel, molecular movement becomes so intensified that the forces holding the particles are overcome, and we have the familiar phenomenon of the "melting" of the gel. Again, nitro-cotton, which is completely gelatinised in a minute or so by a urethane, is converted into a sol in a period ranging from a week down to a few minutes, depending entirely on the degree of mechanical stirring employed, which is in accordance with our theory that a sol is formed by mechanically breaking the orienting bonds between the particles. The third significant fact for the special case of soap is that we have never observed Brownian movement under the ultramicroscope in a soap which we had reason to believe was in the form of gel. Bachmann (*Zeitsch. anorg. Chem.*, 1912, **73**, 125) has made similar observations with gels of gelatin.

This conception explains, moreover, the fact that the apparent viscosity of a sol frequently depends on its previous treatment and history. Many sols must be in process of forming such orientations between their particles, and hence the viscosity must depend on how far this has gone. Thus, for instance, a sol of boiled starch, the delicate incipient structure of which had been destroyed by previous shearing, exhibited thereafter much lower viscosity (Hatschek, *Kolloid Zeitsch.*, 1913, **13**, 881). Again, it is quite clear why supersaturation and hysteresis with regard to gelatinisation so frequently occur.

Once more this conception links up with the observed facts of liquid crystals. It would seem that there must be some connexion between the orienting forces observed in crystalline liquids and in gels. Indeed, one of the typical soaps, ammonium oleate, is a well-known liquid crystal. Reference may also be made to Sandqvist's bromophenanthrenesulphonic acid, which is obviously also a colloidal electrolyte, the solutions of which, however, can be obtained under certain conditions as crystalline liquids.

Vorländer has observed that long molecules are required for forming liquid crystals, which agrees with Bose's theory of swarms of long molecules. The same appears to be true of colloidal electrolytes, such as sodium palmitate or hexadecylsulphonic acid. A

decoate in concentrated solutions is a colloidal electrolyte; on the other hand, sodium and naphthalene-α- and -β-sulphonates, and sodium naphthionate, with an equal number of carbon atoms, contain only a small amount of colloid, if any.

The tendency of soaps to form long strings of molecules * or of colloidal particles is demonstrated by the long, ultramicroscopic fibres which are the characteristic feature of curds (and possibly gels) of sodium soaps (observations of Darke, McBain, and Salmon). An exceedingly fine, filamentous structure may account for the elasticity of gels † and also for the fact that they exhibit more or less clearly oriented properties, such, for instance, as the lenticular (that is, not isotropic) form of bubbles generated within gels, as described by Hatschek. Freundlich has published an interesting study of vanadium pentoxide sols which had been aged many years, and in which he found that, at the boundaries or throughout the sol, when the sol was set in movement, all the anisotropic and other characteristics of a crystalline liquid were exhibited.

The theory of gels here deduced also leads to a prediction of the characteristic phenomenon of syneresis. Thus, if there is an orienting force between the particles, there must necessarily be in that force a component of attraction, and hence the gel structure of oriented particles must exhibit a distinct tendency to shrink. Even if this attractive force is only feeble, it must in course of time produce syneresis, since in dilute gels it is opposed only by the viscosity of a fluid. The swelling of gelatin salts is not in conflict with this view, because the ionic micelle of gelatin and proteins, unlike that of soap, does not become crystalloidal in dilute solution, and so continues to be retained within the gel.

The question now arises as to what are the colloidal particles which are linked together in the case of soap to form the gel structure. There are but two possibilities, neutral colloid and ionic micelle. It is uncertain as to how much of the neutral colloid is included in the ionic micelle, and it is just possible,

* It might explain the fact that true reversible equilibria obtain in soap solutions if each of the true colloidal particles of soap were essentially composed of strings or even sheets of molecules, thus harmonising colloidal behaviour with molecular reactivity, and also resolving the problem of the number of phases present in a gel. The mechanical properties of the sols would, however, require further consideration. Indeed, the stable existence of any colloidal aggregate has not yet been explained.

† Each of the innumerable threads consisting of colloidal particles stuck together could exhibit mechanical elasticity in itself. Owing to the amicroscopic degree of dispersion, there would be such great frictional resistance to their displacement in the liquid that this property of elasticity would be transmitted to the mass of gel itself for a temporary period; the time of relaxation would be dependent upon the viscosity of the intramicellar liquid.

although unlikely, that all of it is so included, and that therefore these conducting particles are those the orientation of which gives to the gel its structure. Were this possibility to be entertained, it would have to be assumed that the gel structure as a whole would carry half the current, the corresponding sodium ions being merely interspersed in the intramicellary liquid of the gel.

Much more probably, the neutral colloidal particles are thus linked up. An important fact to remember in the case of soap gels, and one that distinguishes them from salt solutions which have gelatinised with gelatin or agar-agar, is that here more than half the current is carried by the ionic micelle instead of by ordinary ions. Thus these colloidal particles, under the influence of electrical, as distinguished from mechanical, forces must pass as freely through the open network of the gel as they do through the sol. This is quite consonant with the fact that the neutral colloidal particles in soap sol and gel are identical in nature and amount. It is also supported by the observation of Salmon (*loc. cit.*) that the diffusion potential of soap against a solution of chloride is the same for a gel as for the sol, which indicates that the diffusibility of both sodium ion and ionic micelle are unaffected by gelatinisation.

The Theory and Structure of Soap Curds.

Whereas sol and gel are identical, save for some coherence or orientation of the colloidal particles, curds, as will be shown, are the result of an actual removal of soap from the solution in the form of white fibres, the product of a process closely related to crystallisation.

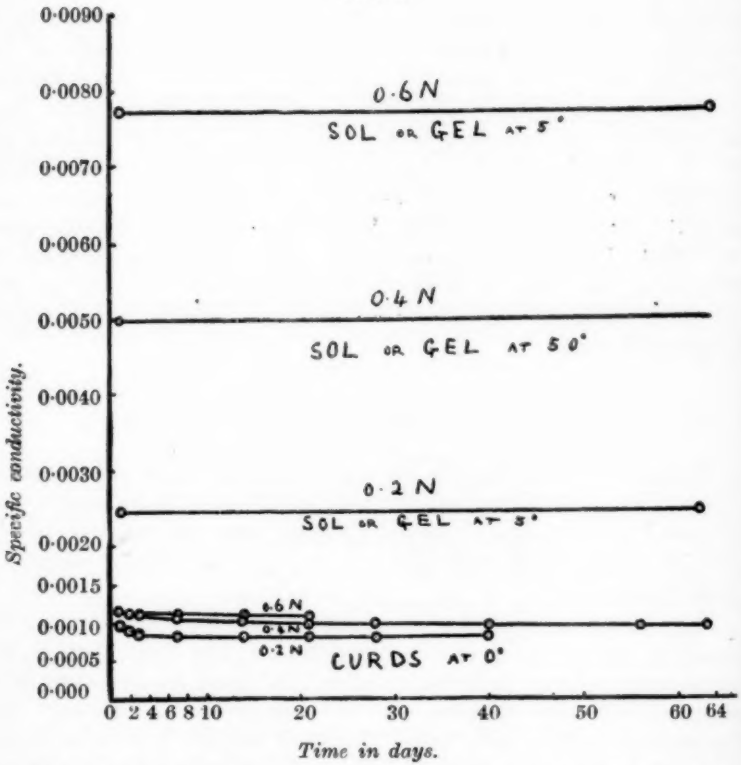
Figs. 1 and 2 show that the specific conductivity of gel or sol is nearly proportional to its concentration, and that that of the corresponding curd is much smaller, and that in the curd it is comparatively independent of the concentration at any one temperature. The curd fibres therefore enmesh a solution much more dilute than the original sol or gel, of concentration which is roughly fixed for any one temperature.

Were curd fibres a true crystalline phase of constant composition, it would follow that the solution they enmesh would exhibit a definite saturation concentration for each temperature, and this concentration would be the definite solubility of such curd fibres at that temperature. The specific conductivity of a curd at any temperature would then be nearly independent of the total original concentration of that curd, although only approximately so, on account of the mechanical diminution of the cross-section of

the electrolyte through the presence of masses of curd fibres in concentrated curds. One would expect, for this reason, that the conductivity of a concentrated curd would be low as compared with that of a dilute curd. The contrary is, however, the case. The conductivity of a 0·6*N*-curd is always distinctly *greater* than that of a 0·2*N*-curd, and it is sometimes nearly twice as great.

Again, for a true crystalline phase of constant composition, the

FIG. 1.



Specific conductivities of 0·2-, 0·4-, *and* 0·6*N-curds, gels, and sols o sodium oleate, showing relative magnitude and effect of time.*

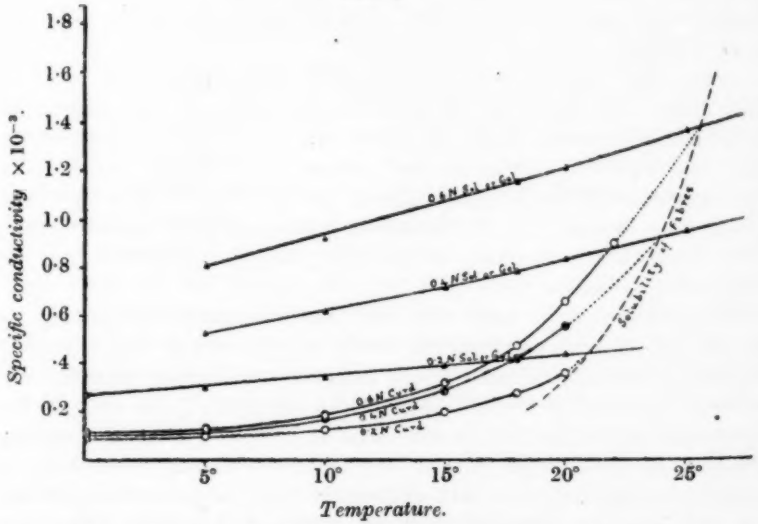
solubility would be independent of time, whereas for curd fibres this is not so. The curd falls off rapidly in conductivity during the first twelve hours, and the conductivity continues to diminish slowly for some months. As shown in table VI and Fig. 2, the conductivity of 0·2*N*-curd fell steadily for fourteen days, then remained nearly constant up to forty days at 0°. The 0·6*N*-curd was altering so slowly that the experiment was discontinued at

twenty-one days, but the later experiment, with 0·4*N*-curd, where the conductivity was still falling at sixty-three days, shows that changes must extend over a period of months at least.

Hence, although formation of curd means the separation of neutral soap from solution in the form of curd fibres, and is analogous to crystallisation, these fibres constitute a variable phase. For the present case, the phase rule assumes the form $P+F=C+3$, where the extra degree of freedom is the diameter of the component particles of the curd fibre, or the diameter of the fibres themselves if each of these is one solid whole.

There are two possible factors of variability, namely, the

FIG. 2



Specific conductivity of sols, gels, and curds of sodium oleate at various temperatures.

diameter of the fibres and their degree of hydration. The first factor ceases to cause appreciable change as soon as the fibres have become microscopic. In any case, it can scarcely be the chief factor here concerned, for the specific conductivities of fresh 0·2 and 0·4*N*-curds differ too greatly, whilst those of 0·4 and 0·6*N*-curds, which at first nearly coincide, diverge on keeping, although by hypothesis the mother liquor would be identical in both cases. The general nature of the facts in tables III to VII is the same, whether fresh or aged curds are considered, whether equilibrium is approached from one side or the other, and whether much or but little time has been taken in so approaching equilibrium.

It would appear that the important factor involved is degree of hydration, and that the more heavily hydrated fibres are the more insoluble and the more stable. Taking the last point first, it follows from the phase rule that for any definite diameter of fibre (or of component particles), the most stable form is that which is least soluble, and, in fact, the conductivity does diminish with time.

As regards degree of hydration, a series of investigations in this laboratory, using several methods, one of which has been published (McBain and Taylor, T., 1919, **115**, 1300), has shown that hydration of curd fibres is greatly influenced by the vapour pressure of the mother liquor. Thus in the presence of 3·0*N*-sodium hydroxide the composition of the palmitate fibres was $NaP,3{\cdot}2H_2O$, whilst in the presence of 1·5*N*-sodium hydroxide it was $NaP,6{\cdot}5H_2O$.

According to this, therefore, the curd fibres which first separate out from 0·6*N*-oleate sol or gel are less hydrated and also more soluble than fibres which separate from 0·2*N*-oleate. Such fibres are, moreover, unstable, in that greater hydration is required to correspond with the residual diluted mother liquor with which they are finally in contact. It should be mentioned that concentration, not temperature as such, is the chief factor in determining the degree of hydration.

Equilibrium in a soap curd can therefore only be attained by a process of recrystallisation, with formation of more heavily hydrated fibres, a process which requires much time, since convection or stirring is impossible and the diffusibility of soap is low (Salmon, *loc. cit.*). It seems certain, however, that the concentration of the mother liquor enmeshed in a soap curd kept at constant temperature would ultimately reach a value independent of its original concentration or previous history. This view receives further support from a comparison of tables III or V with VII, which show that an aged 0·6*N*-curd exhibits a lower conductivity than a moderately fresh 0·4*N*-curd; similarly with 0·4*N*- and 0·2*N*-curds. Further, a curd which has been well aged at 0° possesses, on subsequent keeping at any higher temperature, a conductivity which shows no tendency to rise.

Discussing conductivity, as distinguished from concentration, it is a matter for some surprise that the heavy mass of fibres in a 0·6*N*-curd does not cause such mechanical obstruction to the passage of the current through reduction of the effective cross-section of the liquid as to reduce the specific conductivity to a much lower value than that of a 0·2*N*-solution, in which only about one-quarter as much fibre is present. The apparent absence

of any such effect might possibly be due to electric endosmosis; the study of the problem is being continued with the object of elucidating the phenomena which accompany the passage of current in gels and sols as well as curds. The conductivity data here given suffice to show that if the two effects suggested are appreciable they nearly counterbalance each other.

The conductivity curves in Fig. 2 show that with rising temperature the solubility of the curd fibres increases, and the conductivity rapidly rises towards that of the sol or gel. The conductivity of curd, sol, and gel will become identical at the point where the solubility of the soap fibres becomes equal to the gross concentration of soap present, where the last fibre just dissolves, or where the first fibre just appears. Such a solubility curve is indicated by the line of dashes in Fig. 2, although its exact position varies somewhat with the previous history of the curd fibres present.

The rapid increase of the solubility of the curd fibres with rise of temperature is in accordance with that required by thermodynamics, as deduced from the heat of solidification. The heat evolved on solidification in the case of a soap solution which has been cooled well below the temperature of initial solidification results in a noticeable rise of temperature.

This conception of the solidification of soap solution as being essentially of the nature of a crystallisation process, with separation of curd fibres, also explains the observation of McBain and Martin with regard to the increased alkalinity of curds at low temperatures as compared with sols at somewhat higher temperatures. They found that the hydrolytic alkalinity of the sol increases, within certain limits, with decrease of concentration or with rise of temperature. That it is greater when curd has formed is now evidently due to the fact that the residual solution is more dilute, and hence more hydrolysed. It is thus not necessary to conclude that the fibres in soap curd are anything but neutral (hydrated) soap, whereas previously it might have been suspected that they were very slightly acid soap (see also the analyses below).

The behaviour of the sodium oleate systems here investigated is all in agreement with the incidental observations of McBain, Cornish, and Bowden on sodium myristate (T., 1912, **101**, 2053), only they, like all authors hereto, confused gels and curds, and they did not allow sufficient time in the measurements of curds. They concluded that the formation of a soap curd is not a process continuous with the adjustment of the degree of dispersion of a colloid in the sol, since in a sol, supersaturated with respect to formation of curd, true reversible equilibrium subsists.

Composition and Solubility of Curd Fibres.

In order to obtain a direct experimental control of the deductions made on the preceding section, curds and mother liquor were analysed. From curds of 0·6*N*-oleate, as much as possible of the enmeshed mother liquor was removed by pressure and suction in an atmosphere free from carbon dioxide, and the amounts of sodium and fatty acid radicle were determined. Three specimens thus examined all showed a slight alkalinity, the proportion of sodium to fatty acid radicle being 100·4, 100·9, 100·4 equivalents of sodium to 100 equivalents of oleic radicle. This slight alkalinity may be attributed to oxidation of the oleate. It is thus established that the curd fibres consist essentially of (hydrated) neutral soap; the small amounts of acid soap which correspond with the hydrolytic alkalinity of all soap solutions are evidently completely submerged in these high concentrations of these neutral soap fibres. No data previously existed with regard to this point, for although many authors had analysed the sediments and suspensions from various soap solutions, since these always referred to low concentrations of solid, they found acid soaps of varying composition.

Analyses made of the mother liquor of 0·6*N*-curd at various temperatures also showed equivalence of the sodium and oleic radicle within a small fraction of 1 per cent. Each of these determinations was carried out in duplicate, involving four independent analyses for each case. The resulting solubilities thus determined are, for 0·590*N*-curd of sodium oleate about sixteen hours old, 0·391*N* at 18° and 0·261*N* at 10°, and for 0·1905*N*-sodium oleate and of about the same age at 18°, 0·0998*N*. The solubility obtained from a 0·590*N*-curd, after three days at 0°, was 0·114*N*.

These analyses thus substantiate the conclusions of the preceding section, and the lack of quantitative agreement with the conductivity measurements must partly, at least, be attributed to the difference in the age and previous history of the respective specimens. Further measurements will be undertaken with well-aged curds, the conductivity of which will be taken just before analysis.

Preliminary Experiments on the Behaviour of Mixed Curds of Oleate and Palmitate.

In view of the fact that all commercial soaps are made from mixtures of fatty acids, it is of importance to inquire as to whether these different sodium salts separate out independently or whether the individual fibres are each composed of mixture of soaps. It

will be seen that although to a large extent the oleate and palmitate remain independent, the separation is nevertheless incomplete. Sodium palmitate was chosen, because its molecular weight, and especially its iodine value, differ from those of the oleate, and because its solubility is less than $N/40$ at 25—30°, temperatures at which sodium oleate does not exist in the form of curd.

Equivalent quantities of solutions of the oleate and palmitate were melted together to form a clear sol, and then allowed to cool until curd fibres separated out.

In the first experiment, the enmeshed liquor was withdrawn at 35°, by means of a pipette, to a tiny piece of filter paper, which withheld the soap and allowed the soap solution to pass. The liquor was then weighed for analysis.

In the second experiment, the mixed soap curd was transferred at 30° to a vacuum filter, and the enmeshed liquor drawn through. Air passing through the soap caused frothing of the withdrawn liquor. This was condensed by warming the flask, and weighed for analysis.

In the third experiment, the treatment was similar to that in the second, except that air deprived of carbon dioxide was drawn through the soap, the temperature this time being 25° (but see below).

In the second and third cases, comparative experiments were made with aqueous sodium palmitate of the same concentration as in the mixture to ascertain what concentration of the more insoluble sodium palmitate existed at that temperature in the enmeshed liquor.

The total concentration of soap in the filtrate was determined by decomposing and titrating with aqueous acid as well as with alcoholic hydroxide; the molecular weight of the fatty acid was deduced from its weight and the latter titration, and, finally, the iodine value of the fatty acid was determined.

TABLE IX.

Analysis of Mother Liquor in Mixed Curd of Sodium Oleate and Palmitate.

Experiment.	Temperature.	Concentration.	Filtrate.	Mol. wt.*	Iodine value.†
1...	36°	0·1680*N* each	0·1732*N*	286·9	82·2
2...	30—35	0·1903*N* each	0·2303*N*	279·8	71·8
2...	30	0·1914*N* NaP	0·01778*N*	256·3	—
3...	25—17	0·2486*N* each	(0·2152*N*)	282·7	*81·2*
3...	25	0·2500*N* NaP	0·00819*N*	—	—

* H P = 256·1 by theory; H Ol = 282·3 by theory
† H P = 0 0 by theory; H Ol = 90·1 by theory; see table I.

Table IX shows that most of the oleate remains in the mother liquor, and that the palmitate mostly separates out as curd fibres. This is shown by the high iodine values of the mixed fatty acids in the filtrate, namely, 82, 72, and 81, comparable with fairly pure oleic acid, as was shown in table I.

The separation is, however, not quite complete, for there is some oleate in the curd fibres. This was shown by a continuation of experiment (3), in which the residual curd was washed with pure water, and then a sample tested for the molecular weight of the fatty acid in the curd fibres. The result was 263·1 instead of the theoretical value 256·1 for palmitic acid. After about half of the curd had been washed away, a sample was taken for determination of the iodine value of the fatty acids present. The result was 11·2 instead of the 3·0 for the original palmitic acid used. Hence the palmitate fibres contained 10—20 per cent. of oleate also, although, unfortunately, at the end of this experiment the temperature was low enough for oleate itself to curd. It is fortunate that the behaviour of a mixture is even so far additive, since in the corresponding sol the behaviour is much more complex. Further experiments at exact temperatures are contemplated.

Characterisation of a Commercial Soap.

It is now possible to attempt a definition of a commercial soap. A transparent soap is a gel. All other hard commercial soaps are gels containing a felt of curd fibres. The gelatinisation may be due to the dissolved soaps or it may be partly due to other gelatinising filling agents. Curd fibres enmeshing a sol instead of a gel would probably not have the physical properties required.

Thus, some of the soap is separated out as curd fibres, whilst some is in solution. The latter is absolutely necessary if the soap is to exhibit detergent action at ordinary temperatures. A soap containing only palmitate and stearate would not be a detergent at ordinary temperatures. The value of the presence of oleate lies, not only in its solubility, but in the persistence of its colloidal constituents in unusually dilute solutions.

A good illustration of the dual qualities required of a commercial soap is to be found in the behaviour of remnants of used soaps which have largely lost their detergent properties through extraction of the more soluble constituents.

Holde (*Chem. Umschau Fett. Ind.*, 1920, **27**, 56; *Seifenfabr.*, 1920, **40**, 113), in a recent summary of the facts with regard to residues of soap cakes, considers the further factor which helps in the accumulation of insoluble matter in these residues, namely,

the precipitation of calcium salts through reaction with the impurities in the water.

Further interesting corroboration of the views here put forward is observed in the formation of the feathery clusters which separate in a soft soap on keeping, known as figging. Soft soaps made from linseed oil (and therefore containing chiefly very soluble soaps if unsaturated fatty acids show no "fig"). A small proportion of tallow rich in the less soluble stearate ensures figging.

Another example is that mentioned by "H.A." (*Seifensied. Zeit.*, 1920, **47**, 646). A sodium soap made from coconut oil alone is very hard and very crumbly. Substitution of potassium for some of the sodium, together with the addition of some potassium chloride to develop formation of a colloid, makes this soap more like ordinary soap, so that it can be stamped out into cakes.

For completeness, it should be mentioned that many commercial soaps are formed by the curding of a mixture of two liquids. When salt is added to a soap solution, the viscosity rises enormously, until suddenly the solution breaks into two layers and the mixture becomes of manageable effective mobility in the soap pan.

Thus normally in the process of soap boiling the soap is probably never allowed to be in one homogeneous solution. This statement is the subject of a further communication from this laboratory to be made by Mr. Burnett.

Summary.

(1) We have discovered that a soap solution of one and the same concentration at any definite temperature may be prepared in three characteristic states; namely, clear fluid sol, transparent elastic gel, and white opaque curd. The latter has often, but erroneously, been called a gel.

(2) The sol and gel forms of a solution of sodium oleate are identical in osmotic activity, concentration of sodium ions, conductivity, and refractive index; this proves that identical chemical equilibria and constituents are present in the two cases. The sol and gel differ only through the mechanical rigidity and elasticity of the gel form.

(3) The quantitative identity of conductivity in sol and gel is irreconcilable with all theories of gel structure hitherto advanced, with the exception of the micellar theory of Nägeli, which was resuscitated by Zsigmondy and Bachmann in 1912, and is strongly supported by many lines of evidence referred to in the present

paper. The colloidal particles in sol and gel are the same, but whereas in the former they are independent, in a fully formed gel they stick together, probably to form a filamentous structure. It is probably the particles of neutral soap, and not of ionic micelle, that exhibit this behaviour.

(4) The formation of soap curd, in clear contradistinction from gelatinisation, is analogous to a process of crystallisation, neutral soap separating from the solution in the form of curd fibres of microscopic or ultramicroscopic diameter. This is shown by the drop in conductivity and osmotic activity, and confirmed by direct and indirect analysis in addition to observations with the ultramicroscope. Coagulation and crystallisation are thus sharply distinguished from gelatinisation. This we consider to be the chief theoretical result of the present paper.

(5) The curd fibres consist of hydrated neutral soap, the hydration of which depends on their origin and previous history. Within corresponding limits, their solubility is definite for each temperature. The so-called melting points of soap curds are the temperatures at which the solubility curve rises to a value equal to that of the total concentration of the soap, and at which the last curd fibre just dissolves.

(6) All the above results are of general applicability, both on account of the detailed similarity of soaps to protein and gelatin salts, etc., as well as on account of the precision of the methods available in the investigation of these simple systems.

(7) In a curd formed from a mixture of palmitic and oleic acids, the two soaps are largely independent.

In conclusion, our thanks are due to the Colston Society of the University of Bristol, and to the Research Fund of the Chemical Society, for their generous grants, which enabled this work to be carried out.

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BRISTOL.

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CLXVIII.—*A New Method for the Preparation of 2 : 4-Dihydroxy- and 2 : 4 : 4′-Trihydroxy-benzophenone, and some Observations relating to the Hoesch Reaction.*

By Henry Stephen.

In Hoesch's method (*Ber.*, 1915, **48**, 1122) for the preparation of aromatic hydroxy-ketones by condensing phenolic compounds with nitriles in the presence of hydrogen chloride, the formation of an imino-chloride, CRCl:NH, is assumed, and this compound condenses with the phenolic compound to yield the ketimine, CRR′:NH. The latter yields the corresponding ketone on hydrolysis. Cyanogen bromide is exceptional in its behaviour towards hydrogen chloride (compare Karrer, *Helv. Chim. Acta*, 1919, **2**, 89). References to the formation of additive compounds (imino-haloids) of nitriles and hydrogen haloids are given in the literature (Gauthier, *Annalen*, 1869, **150**, 187; Michael and Wing, *Amer. Chem. J.*, 1885, **7**, 71), but the most definite evidence of the formation of such additive compounds was obtained by Tröger and Lüning (*J. pr. Chem.*, 1904, [ii], **69**, 347), who obtained chloroacetimide chloride, $CH_2Cl{\cdot}CCl{:}NH$, from chloroacetonitrile and hydrogen chloride. The author has prepared this compound, and found that, on mixing it with the theoretical amount of resorcinol and warming on the water-bath at 50—60°, hydrogen chloride was evolved, ω-chlororesacetophenone (needles, m. p. 131°) being subsequently isolated from the product. Sonn (*Ber.*, 1917, **50**, 1262) has condensed chloroacetonitrile with resorcinol according to Hoesch's method, and obtained the same substance. The mechanism of the reaction is therefore explained as follows, according to the above experiment:

$$C_6H_4(OH)_2 + CH_2Cl{\cdot}CCl{:}NH \xrightarrow{-HCl} \underset{\text{(I.)}}{C_6H_3(OH)_2{\cdot}C(:NH){\cdot}CH_2Cl},$$

the ketimine (I) yielding the ketone on hydrolysis.

Further evidence of the mechanism of the Hoesch reaction is afforded by the fact that certain *N*-substituted imino-chlorides, for example, benzanilideiminochloride, CPhCl:NPh, react on warming with resorcinol, yielding the anils of the corresponding hydroxy-ketones. Thus, in the case of benzanilideiminochloride, the anil

(II) of 2:4-dihydroxybenzophenone is obtained as follows, and, on hydrolysis, yields the ketone:

$$C_6H_4(OH)_2 + CPhCl{:}NPh \xrightarrow{-HCl} \underset{(II.)}{C_6H_3(OH)_2{\cdot}CPh{:}NPh}.$$

In a similar way, 2:4:4′-trihydroxybenzophenone,

$$OH{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_3(OH)_2$$

(III), was obtained from *p*-ethylcarbonatobenzanilideiminochloride (Sonn and Müller, *Ber.*, 1919, **52**, 1927).

An attempt to prepare 2:4-dihydroxyphenyl styryl ketone* by condensing cinnamanilideiminochloride with resorcinol was unsuccessful.

It may be mentioned that cinnamanilideiminochloride, prepared according to Sonn and Müller's method (*loc. cit.*), is a solid crystallising from toluene in clusters of needles melting at 30°, and not a red, viscous mass, as described by these authors, although if heated for some time on the water-bath the crystals change into a red mass.

The failure to prepare 2:4-dihydroxyphenyl styryl ketone is parallel to that of Fischer and Nouri (*Ber.*, 1917, **50**, 693), who attempted to prepare 2:4:6-trihydroxyphenyl styryl ketone from phloroglucinol and cinnamonitrile by Hoesch's method, and obtained instead 5:7-dihydroxy-4-phenyl-3:4-dihydro-1:2-benzopyrone. This anomalous behaviour is due, apparently, to the unsaturated nature of the nitrile, since phloretonitrile (*β*-*p*-hydroxyphenylpropionitrile) condenses in the usual way with resorcinol or phloroglucinol.

In carrying out the condensations of the *N*-substituted iminochlorides with resorcinol, certain observations have led the author to believe that an imino-ether is the first product of the reaction, which then undergoes isomeric change, resulting in a shift of the group ·CPh:NPh into the nucleus in the ortho- and para-positions with respect to the hydroxyl groups. Thus, in the case of benzanilideiminochloride, the preliminary reaction may be represented

* This ketone cannot be prepared by condensing resorcinol and cinnamonitrile according to Hoesch's method for reasons which are given later. Bargellini and Marantonio (*Atti R. Accad. Lincei*, 1908, [v], **17**, ii, 119) state that the same ketone can be prepared by fusing cinnamic acid and resorcinol with anhydrous zinc chloride. This experiment was repeated in order to obtain a specimen of the ketone for purposes of comparison, and the details are so simple that no difficulty would be anticipated. After many attempts had been made, the method was abandoned, no trace of ketone being obtained, the chief result being the formation of a red-coloured substance the investigation of which was not pursued further, and the conclusion was drawn that the statement of the above authors was incorrect.

as follows, the imino-ether (IV) undergoing subsequent change to yield the anil (II):

$$C_6H_4(OH)_2 + CPhCl{:}NPh \xrightarrow{-HCl} \underset{\text{(IV.)}}{C_6H_3(OH)\cdot O\cdot CPh{:}NPh}.$$

The evidence in favour of this isomeric change depends on the observation that the best yield of the anil (II) was obtained by first warming the mixture of the imino-chloride and resorcinol on the water-bath until the evolution of hydrogen chloride ceased, and subsequently heating in an oil-bath at 150°. Several instances of isomeric change of acyl derivatives of phenols involving a migration of the acyl group into the nucleus are also known to take place on heating. The preliminary warming of the above mixture on the water-bath resulted in the formation of an oily product, which was found to be easily hydrolysed into benzanilide and resorcinol on boiling for a short time with dilute hydrochloric acid; this would be the behaviour expected of the imino-ether.

A similar observation was made in experiments with cinnamanilideiminochloride and resorcinol, and it is probable that the imino-ether (V) is first formed on the water-bath, but, on heating at a higher temperature in an oil-bath, this undergoes internal condensation, and not the above isomeric change, yielding the anil of 7-hydroxy-4-phenyl-3:4-dihydro-1:2-benzopyrone (VI):

$$\underset{\text{(V.)}}{C_6H_4(OH)\cdot O\cdot C(:NPh)\cdot CH{:}CHPh} \xrightarrow{\text{heat}} \underset{\text{(VI.)}}{C_6H_3(OH)\begin{cases} CHPh\cdot CH_2 \\ O\text{——}C{:}NPh \end{cases}}.$$

This reaction is thus analogous to the formation of the benzopyrone investigated by Fischer and Nouri (*loc. cit.*). The imino-ether (V) was obtained as an oily product, which was easily hydrolysed to cinnamanilide and resorcinol on boiling for a few minutes with dilute hydrochloric acid or by prolonged boiling with water. The formation of the anil (VI) still remains in doubt, and is reserved for further investigation.

EXPERIMENTAL.

2:4-*Dihydroxybenzophenone* (*Benzoresorcinol*).

The benzanilideiminochloride used in this experiment was prepared from benzanilide which had been carefully purified. The method adopted was the same as that due to Wallach (*Annalen*, 1877, **184**, 86), and the product was purified by distillation under diminished pressure. Attempts were made to replace the phosphorus pentachloride as used in Wallach's method by thionyl chloride, but without success.

Three grams (1 mol.) of the imino-chloride were mixed with 2 grams (1 mol.) of resorcinol, and then warmed on the water-bath at 50°; when the evolution of hydrogen chloride had ceased, the mixture was transferred to an oil-bath and heated for ten minutes at 150°. Longer heating caused much decomposition, the product becoming darker in colour. The red-coloured mass was then boiled with water to remove any unchanged resorcinol, and the aqueous solution decanted from the viscid, red oil. This operation was repeated several times, and the oil allowed to remain in the refrigerator overnight. It showed no tendency to crystallise, being very readily soluble in most of the usual solvents. After several attempts, a small quantity of a bright yellow, crystalline compound separated from ethyl acetate, which melted and decomposed at 228—230°. There was, unfortunately, insufficient for an analysis.

Hydrolysis of the Anilide of 2:4-*Dihydroxybenzophenone.*

The most successful method of hydrolysis consisted in boiling the oil with about 25 per cent. hydrochloric acid. The oil was first treated with 50 c.c. of hydrochloric acid, boiled for fifteen minutes, and the yellow solution decanted and filtered from the tarry matter. This operation was repeated several times, the accumulated filtrates were boiled with animal charcoal, and, on filtering, a clear solution was obtained, from which long needles of 2:4-dihydroxybenzophenone separated. These melted at 144°, and were identical with a sample of the same substance prepared by condensing benzonitrile with resorcinol according to the method used by Hoesch, who prepared the substance in that way.

A more rapid method of hydrolysis, but one which leads to difficulty in the final stage of purification of the product, consists in heating the oil with sufficient dilute alcohol to dissolve it, and then passing in hydrogen chloride until the solvent is nearly saturated. The mixture was boiled for a whole day under a reflux condenser, and then filtered. Some tarry matter passed into the filtrate, owing to the alcohol present, and this causes difficulty in the purification of the ketone after evaporation of the alcohol, but by recrystallising the product several times from hot water and repeated treatment with animal charcoal, a pure sample of 2:4-dihydroxybenzophenone was obtained.

2:4:4′-*Trihydroxybenzophenone* (III).

The starting material for the experiment was *p*-ethylcarbonatobenzoic acid, which was prepared according to Fischer and

Freudenberg's method (*Annalen*, 1910, **372**, 36), by shaking 30 grams of *p*-hydroxybenzoic acid with 30 grams of ethyl chloroformate and 450 c.c. of *N*-sodium hydroxide. It crystallised from acetone in needles melting at 156°.

The acid chloride was prepared by heating 25 grams of the acid with 24 grams of phosphorus pentachloride. After removing the phosphoryl chloride, the acid chloride distilled at 170°/12 mm.

It was then converted into *p*-ethylcarbonatobenzanilide by dissolving 20 grams in dry benzene and gradually adding 17 grams (2 mols.) of aniline while shaking. A white solid, consisting of a mixture of aniline hydrochloride and *p*-ethylcarbonatobenzanilide, separated, and, after allowing to remain overnight, the precipitate was collected and triturated with very dilute hydrochloric acid to remove aniline hydrochloride. It was then collected, washed with water, then with dilute sodium hydrogen carbonate solution to remove any acid present, and again with water, and then dried.

Preparation of the Imino-chloride.

Five grams (1 mol.) of *p*-ethylcarbonatobenzanilide were suspended in dry toluene, 3·7 grams (1 mol.) of powdered phosphorus pentachloride added, and the mixture was warmed gently on the water-bath for fifteen minutes, when a clear solution was obtained. The phosphoryl chloride and toluene were then distilled off under diminished pressure, and the imino-chloride remained as a brown, crystalline mass. This was not purified, as it easily decomposes in air, but it melted at about 80°.

Condensation of Resorcinol with the Imino-chloride.

To the imino-chloride in the distillation flask, 2·5 grams (1 mol.) of resorcinol were added, and the mixture was warmed gently on the steam-bath. A reaction soon started, hydrogen chloride being evolved, and the mass became darker in colour. After heating for twenty minutes, the residue was dissolved in alcohol, about 2 c.c. of hydrochloric acid were added, and the mixture was boiled for several hours in order to hydrolyse the ethylcarbonato-group and the imino-group. The alcohol was then distilled off under diminished pressure, and the residue crystallised from hot water in pale yellow needles melting at 200°. It gave a purple coloration with ferric chloride in alcoholic solution, and was found to be 2:4:4′-trihydroxybenzophenone (Komarowski and Kostanecki, *Ber.*, 1894, **27**, 1999, give the melting point as 200—201°).

The author desires to express his thanks to Miss L. Higginbotham and Mr. W. K. Slater for assistance with certain parts of the experimental work.

THE CHEMICAL DEPARTMENT,
THE UNIVERSITY,
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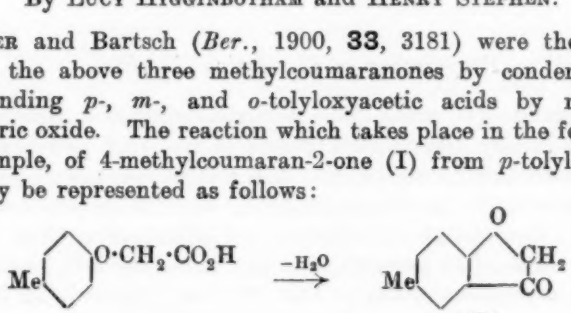
CLXIX.—*Studies in the Coumaranone Series. Part I. The Preparation of* 4-, 5-, *and* 6-*Methylcoumaran-2-ones, and some Derivatives of* o-, m-, *and* p-*Tolyloxyacetic Acids.*

By LUCY HIGGINBOTHAM and HENRY STEPHEN.

STOERMER and Bartsch (*Ber.*, 1900, **33**, 3181) were the first to prepare the above three methylcoumaranones by condensing the corresponding *p*-, *m*-, and *o*-tolyloxyacetic acids by means of phosphoric oxide. The reaction which takes place in the formation, for example, of 4-methylcoumaran-2-one (I) from *p*-tolyloxyacetic acid may be represented as follows:



(I.)

Poor yields of the coumaranones were obtained by the above method, and the compounds isolated, and certain derivatives of them, were impure, as subsequent investigation has shown. The preparation of 4-methylcoumaranone (I) was carried out successfully by Auwers and Müller (*Ber.*, 1908, **41**, 4233) and Fries and Finck (*ibid.*, p. 4271) almost simultaneously, and the latter authors also describe the preparation of 5-methylcoumaranone.* The method in both cases depends on the withdrawal of the elements of hydrogen haloid from ω-halogen-*o*-hydroxyacetophenones, but, owing to the difficulty in obtaining the required acetophenones, the method is not suitable for more general application.

The present investigation provides a method for the preparation of all three coumaranones, and is in principle analogous to the method given by Stoermer and Bartsch indicated above, but with

* Auwers (*Ber.*, 1916, **49**, 809) has recently prepared 6-methylcoumaran-2-one by a similar method.

the difference that the coumaranones are derived from the acid chlorides of the three tolyloxyacetic acids. Methods for the preparation of these acids have been known for some time, but modifications of them are described in the present paper which give improved yields and shorten the time required for reaction. The conversion of the acids into the acid chlorides was found to take place more readily using thionyl chloride rather than phosphorus pentachloride. Michael (*Amer. Chem. J.*, 1889, **9**, 216) has shown that phenoxyacetic acid, on treatment with phosphorus pentachloride, yields the acid chloride, but, at the same time, a considerable amount of a mixture of *o*- and *p*-chlorophenoxyacetyl chlorides is formed. Using thionyl chloride, almost quantitative yields of the three tolyloxyacetyl chlorides are obtained. Phenoxyacetyl chloride is also readily prepared in this way.

Stoermer and Atenstadt (*Ber.*, 1902, **35**, 3569) have shown that when phenoxyacetyl chloride is dissolved in benzene and treated with aluminium chloride, two products result from the reaction, namely, coumaran-2-one (m. p. 101°) and ω-phenoxyacetophenone (m. p. 72°). These were separated, according to the above authors, by distillation in a current of steam, coumaran-2-one being volatile and ω-phenoxyacetophenone being isolated from the residue after distillation. This procedure is not, however, in agreement with the statement of Möhlau (*Ber.*, 1882, **15**, 2497), who prepared ω-phenoxyacetophenone (m. p. 72°) from ω-bromoacetophenone and phenol in alkaline solution, and describes the ketone as being volatile in steam. It is thus difficult to understand how Stoermer and Atenstadt could have isolated the ketone in the manner described. A repetition of their experiment has been made, and, whilst no ketone was isolated, a small amount of coumaran-2-one was obtained (m. p 101°). The latter substance was also isolated from the reaction which took place when a solution of phenoxyacetyl chloride in carbon disulphide was treated with aluminium chloride. In both cases, much residue was left after distillation with steam.

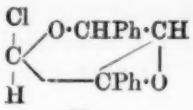
The above reaction was then applied to the three tolyloxyacetyl chlorides mentioned above, and in the first series of experiments the reaction was carried out using an excess of benzene as solvent. None of the three ω-tolyloxyacetophenones, which might have been formed in the usual way by the condensation of the tolyloxyacetyl chlorides with benzene, was obtained, the only crystalline products isolated from the reactions being the 4-, 5-, and 6-methylcoumaranones. The same compounds were formed by treating solutions of the acid chlorides in carbon disulphide with aluminium chloride. The yields of coumaranones obtained by either method of procedure are approximately the same, usually about 35 to 40 per

cent. of the theoretical, and although not quite so good as those obtained by Auwers and Müller and by Fries and Finck (*loc. cit.*), the method offers several advantages over that given by these investigators.

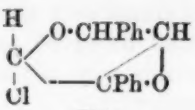
For purposes of comparison, attempts have been made to prepare the three ω-tolyloxyacetophenones according to the method described by Kunckell (*Ber.*, 1897, **30**, 577), who claims to have prepared ω-*m*-tolyloxyacetophenone by treating ω-bromoacetophenone and *m*-cresol dissolved in alcohol with sodium hydroxide, and, in a similar way, ω-*p*-tolyloxyacetophenone was prepared from ω-bromoacetophenone and *p*-cresol. Both experiments were repeated with a slight modification, using ω-chloroacetophenone instead of the corresponding bromo-compound, and from each experiment two substances were obtained, both of which contained chlorine, and melted at 118° and 148° respectively. These compounds were isolated under different conditions, the former being obtained by warming a mixture of ω-chloroacetophenone with either *m*- or *p*-cresol in the presence of alcoholic sodium hydroxide on the water-bath for an hour. After filtering off the sodium chloride formed during the reaction from the alcoholic solution, which no longer possessed the pungent odour of the chloro-ketone, although the odour of cresol was evident, fine needles were deposited which melted as above after recrystallisation from methyl alcohol. The compound of higher melting point was formed when the heating of the alcoholic solution of the mixture was continued for several hours. After similar treatment, the above-mentioned compound, melting at 148° and crystallising from methyl alcohol in small prisms, was obtained. Subsequent investigation has shown that both substances could be obtained in several ways; thus, on treating an alcoholic solution of ω-chloroacetophenone with the dry sodium compounds of phenol, *o*-, *m*-, and *p*-cresols, and β-naphthol, respectively, each experiment gave one or other of the above chloro-compounds, according to the duration of the reaction.

The action of these sodium compounds, and also that of sodium hydroxide, on ω-chloroacetophenone is the same as that of ammonia and sodium ethoxide on the same substance as was investigated by Staedel and Rügheimer (*Ber.*, 1876, **9**, 1759) and by Paal and Stern (*Ber.*, 1899, **32**, 531) respectively, and both investigations have shown that two chloro-compounds are formed, namely, the so-called α- and β-chlorodiphenacyls, melting at 117° and 154° respectively. Widman and Almström (*Annalen*, 1913, **400**, 86) have investigated the constitutions of both compounds, and shown that α-chlorodiphenacyl is *cis*-2-chloro-3:4-oxido-3:5-diphenyltetrahydrofuran (II) (m. p. 117—118°), and that the β-compound is

the corresponding *trans*-isomeride (III) (m. p. 149°, and not 154°, as given above).



(II.)



(III.)

It is thus difficult to understand how various investigators in the past have succeeded in preparing ω-alkylated or ω-arylated acetophenones by the action of sodium compounds of alcohols or phenols on ω-halogenacetophenones. An investigation of this problem is being carried out by one of us.

The preparation of other derivatives of *o*-, *m*-, and *p*-tolyloxyacetic acids is described below.

Experimental.

o-, m-, *and* p-*Tolyloxyacetic Acids.*

The preparation of these acids by treating a mixture of chloroacetic acid and the corresponding cresol with an aqueous solution of sodium hydroxide has been known for some time, the ortho-acid having been first prepared by Oglialoro-Todaro and Cannone (*Gazzetta*, 1889, **18**, 511), and the meta- and para-acids by Oglialoro-Todaro and Forte (*Gazzetta*, 1891, **20**, 508) and Gabriel (*Ber.*, 1882, **14**, 923). Details of a modified method for the preparation of the three acids by the same reaction are given in D.R.-P. 79514 and 85490.

Numerous experiments, carried out according to the details given in the above investigations, have shown that the yields of the acids never exceed 60 per cent. of the theoretical, loss of chloroacetic acid by hydrolysis probably taking place. The present investigation has shown that the effect of hydrolysis can be minimised by adding the cresol, dissolved in alkali hydroxide, to the chloroacetic acid. In the particular case of the meta-acid, the sodium hydroxide was replaced by an equivalent amount of potassium hydroxide, which gave an increased yield of the product; in other respects, the process was the same.

Ninety-six grams (1 mol.) of chloroacetic acid were heated in an oil-bath at 110—120°, and a solution of 108 grams (1 mol.) of the cresol and 100 grams (2·5 mols.) of sodium hydroxide in 400 c.c. of water was slowly added with frequent shaking. The addition of the solution was complete in two hours, when the product, after being cooled to about 40°, was acidified with approximately 2*N*-sulphuric acid. The tolyloxyacetic acid was collected, drained,

and finally washed with 20 c.c. of light petroleum to remove traces of adhering cresol. The weight of crude acid was 140 grams, and a further 10 grams were extracted with ether from the filtrate, the combined yield being 90 per cent. of the theoretical. The acid obtained in this way is pure enough for most purposes without further treatment.

The temperature stated above at which the acidification was carried out is of importance, since the meta-acid undergoes decomposition to some extent by mineral acid at higher temperatures. On the other hand, the sodium salt of the para-acid is only moderately soluble in water at 40°, and the free acid was best obtained by warming the solution to 70°, when the sodium salt dissolved, and slowly adding 2*N*-sulphuric acid at the same temperature until acid.

The acids may be purified by crystallisation from dilute alcohol, and are then obtained in thin, glistening plates, the melting points of which are 151—152°, 102°, and 135° for the ortho-, meta-, and para-acids respectively, agreeing with those given in the literature.

The acids are decomposed into the respective cresol and glycollic acid on distillation in a current of steam, or by boiling with dilute mineral acids, the meta-acid more readily than the para-, the ortho-acid being the most resistant to such treatment.

Preparation of the Ammonium Salts of the above Acids.

In connexion with the preparation of the nitriles of the tolyloxyacetic acids, the ammonium salts were obtained most readily in the following way.

Twenty-five grams of the acid were dissolved in 100 c.c. of dry ether, and the solution was saturated with dry ammonia at the ordinary temperature. The anhydrous ammonium salt separated from the ethereal solution as a fine, crystalline powder.

The ammonium salts of the *o*-, *m*-, and *p*-acids decompose at 126°, 188°, and 177° respectively.

o-, m-, *and* p-*Tolyloxyacetyl Chlorides*, $C_9H_9O_2Cl$.

These acid chlorides have hitherto not been described. Twenty grams (1 mol.) of the acid, previously dried by fusion, were finely powdered and placed in a small flask fitted with a reflux apparatus on a water-bath at 60°; 18 grams (1·5 mols.) of thionyl chloride were added slowly, and the reaction was moderated, if necessary, by removal of the flask from the water-bath. The reaction was complete at the end of fifteen minutes, and a pale yellow liquid remained; longer heating caused the product to darken in colour,

resulting in a poor yield of the acid chloride. The excess of thionyl chloride was removed by distillation on the water-bath at 30° under about 15 mm. pressure, and the residue finally distilled at 10 mm. Twenty grams of each acid chloride were obtained as colourless liquids, the yields being about 90 per cent. of the theoretical, and in all three cases the products were obtained solid.

	B. p./10 mm.	M. p.
o-Tolyloxyacetyl chloride	120°	29—30°
m- „ „	126	19·3
p- „ „	124	17·9

They are all soluble in carbon disulphide, benzene, or ether, and are decomposed by water, yielding the respective acids.

o-, m-, *and* p-*Tolyloxyacetamides*, $C_9H_{11}O_2N$.

(1) Twenty grams of the ammonium salt of *o*-tolyloxyacetic acid were heated under 10 mm. pressure in a distillation flask in an oil-bath at 135°, water passed over, and the reaction was complete when the solid in the flask had liquefied, the amide formed being then at a temperature above its melting point.

In the cases of the ammonium salts of the meta- and para-acids, the temperature of the oil-bath was maintained at 190—200° in consequence of the higher decomposition points. The liquid residue solidified on cooling, and the product crystallised from alcohol.

(2) On warming the acid chlorides with an excess of ammonium carbonate on the water-bath for half an hour, and removing the ammonium chloride formed by triturating the solid mass with cold water and filtering, the amides were obtained pure after crystallisation from alcohol, and identical with those prepared by the first method.

The three compounds were purified for analysis by recrystallisation from benzene, being obtained in stout, rhombic prisms, and the purity of each substance was tested by boiling a known weight with aqueous sodium hydroxide and collecting the ammonia liberated in standard acid. The results were in close agreement with the theoretical values.

	M. p.	M. p.
o-Tolyloxyacetamide.....	127°	128°
m- „	118	111—112
p- „	119	126

The figures in the second column are those given by Forte (*Gazzetta*, 1893, **22**, ii, 526).

The amides are sparingly soluble in cold methyl and ethyl alcohols or benzene, but dissolve readily on warming, and are slowly hydrolysed by boiling with water.

The yields of the amides obtained by both methods are about 90 per cent. of the theoretical.

o-, m-, *and* p-*Tolyloxyacetonitriles*, C_9H_9ON.

The meta- and para-compounds were obtained by Stoermer and Schmidt (*Ber.*, 1899, **30**, 1705) from the oximes of the corresponding tolyloxyacetaldehydes, the former being a yellow liquid (b. p. 254°) and the latter crystallising in needles (m. p. 40°). The *ortho*-compound has not hitherto been described. The three substances are more readily prepared by treating the amides with phosphoric oxide.

Ten grams of the amide were intimately mixed with 10 grams of phosphoric oxide in a distillation flask, and the mixture was warmed in an oil-bath at 120°. When the reaction had begun, the side-tube of the receiver attached to the flask was connected to the pump, and a yellow oil distilled at 130°/10 mm. After fifteen minutes, the temperature of the oil-bath was raised to 150°, and the distillation was complete after a further ten minutes. Six grams of nitrile were obtained in this way.

	B. p./10 mm.	M. p.
o-Tolyloxyacetonitrile.....	133°	yellow oil.
m- „	141	„
p- „	136	38—39°

The nitriles are easily hydrolysed on boiling with aqueous sodium hydroxide, yielding the corresponding acid, and are soluble in the usual organic solvents.

o-, m-, *and* p-*Tolyloxyacetanilides*, $C_{15}H_{15}O_2N$.

These anilides may be readily prepared by the following method. Ten grams (1 mol.) of the acid chloride were dissolved in 100 c.c. of dry benzene in a flask fitted with a reflux apparatus, and 10 grams (2 mols.) of freshly distilled aniline slowly added with vigorous shaking. After cooling, the solid which had separated was filtered, and the benzene solution containing some aniline was evaporated, and the residue added to the main bulk. The whole was then triturated with dilute hydrochloric acid to remove aniline hydrochloride, and finally treated with cold dilute sodium carbonate solution to remove traces of acid. The substance was then crystallised from ethyl alcohol, in which the ortho-compound was the most and the para-compound the least soluble, the meta-compound being moderately soluble. They are readily hydrolysed on boiling with dilute hydrochloric acid.

	M. p.
o-Tolyloxyacetanilide (cubes)	108·5°
m- „ (needles).....	95
p- „ („).....	109

These values are in close agreement with those given by Forte (*ibid.*).

4-Methylcoumaran-2-one (I).

Ten grams (1 mol.) of *p*-tolyloxyacetyl chloride were dissolved in 15 grams (3 mols.) of dry benzene, and 8 grams of finely powdered aluminium chloride slowly added with vigorous shaking, the mixture being cooled in ice. The reaction proceeded slowly, and the solution became dark red, but if the temperature was allowed to rise, the mixture rapidly turned into a dark-coloured, tarry mass, and the yield of cumaranone was considerably diminished, in consequence of decomposition. The red solution, after remaining in the cold for two hours, was poured on powdered ice mixed with hydrochloric acid, and the oil suspended in the water submitted to distillation in a current of steam for several hours until the distillate no longer showed a reducing action with Fehling's solution, and the characteristic odour of the coumaranone was imperceptible. The upper layer of benzene, containing some coumaranone in solution, was separated from the aqueous layer, and the latter was extracted with ether several times to remove coumaranone dissolved in the water. The combined benzene and ethereal extracts were dried over anhydrous sodium sulphate, the solvents removed on the water-bath, and, on cooling, the residue solidified to a mass of fine needles. The substance crystallised from ethyl alcohol in white needles melting at 51°. The yield was 3 grams.

The semicarbazone (yellow needles from alcohol) melted at 228° (heated slowly), and the oxime at 143—144° (Stoermer and Bartsch, *loc. cit.*, give 181° and 144° respectively).

The p-*nitrophenylhydrazone* was obtained by adding a solution of *p*-nitrophenylhydrazine in dilute acetic acid to an aqueous solution of the coumaranone. The hydrazone soon separated as a red, crystalline powder, and, after crystallisation from dilute acetic acid, it melted and decomposed at 230—232° (Found: N = 14·4. $C_{15}H_{13}O_3N_3$ requires N = 14·85 per cent.).

5-Methylcoumaran-2-one was prepared in a manner similar to that described above from *m*-tolyloxyacetyl chloride, and was obtained in needles melting at 85°. The semicarbazone and oxime melted at 208° and 156° respectively. For the latter, Fries and Finck (*loc. cit.*) give 165°, probably a misprint. The p-*nitro*-

phenylhydrazone crystallises from dilute acetic acid in red needles melting and decomposing at 214—216°.

6-*Methylcoumaran-2-one*, prepared from *o*-tolyloxyacetyl chloride, crystallised in needles melting at 88°. The semicarbazone and oxime melted at 227° and 148° respectively, and the p-*nitrophenylhydrazone* (red needles) at 195° with decomposition.

The above coumaranones give purple colorations with ferric chloride, they reduce Fehling's solution on warming, and give an immediate precipitate of silver with Tollens' reagent. On treatment with concentrated sulphuric acid, they dissolve, with the production of an intense red colour, and subsequent formation of tarry matter. On remaining in the air for some time, the crystals of the coumaranones become coated with a bright red-coloured substance, probably an oxidation product. They have a characteristic odour resembling that of hyacinth.

The authors desire to thank Professor Lapworth for facilities placed at their disposal in connexion with this investigation, and also Dr. W. W. Adamson for analysing several of the substances described above.

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CLXX.—*Carbazole-blue and Carbazole-violet.*

By MAURICE COPISAROW.

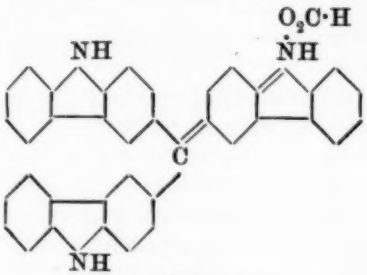
CARBAZOLE-BLUE was first obtained by Suida (*Ber.*, 1879, **12**, 1403) by fusing carbazole with oxalic acid. He regarded it as the internal anhydride of 2-aminodiphenyl-2′-carboxylic acid, whilst Bamberger and Müller (*Ber.*, 1887, **20**, 1903) recognised that its properties pointed to a dye of the triphenylmethane class, and assigned to it the formula $(C_{12}H_8N)_3C{\cdot}OH$, although neither Suida's nor Bamberger and Müller's analytical figures agreed with either of these two formulæ.

The author has now found that carbazole-blue, like the triphenylmethane dyes, furnishes a *carbinol* of the above formula which gives variously coloured salts with acids, of which the formate is identical with the colouring matter in question.

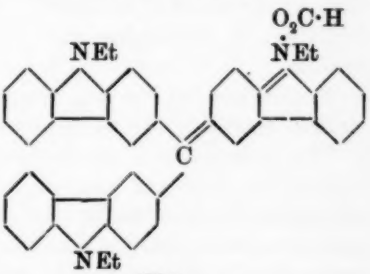
The corresponding *tricarbazylmethane* has also been prepared by reducing carbazole-blue. When 9-ethylcarbazole is similarly

fused with oxalic acid, a corresponding violet colouring matter is obtained, which it is proposed to name *carbazole-violet*, and the *carbinol* and parent *hydrocarbon* of this have been prepared. From analogy to the triphenylmethane dyes, and from the fact that phthalyl chloride and phthalides are intermediate products in the formation of tetraphenylmethane-*o*-carboxylic acids (Copisarow, T., 1917, **111**, 10), just as keto-chlorides are intermediate in the formation of the triphenylmethane dyes from carbon tetrachloride (Fierz and Koechlin, *Helv. Chim. Acta*, 1918, **1**, 218), and, further, that the attachment of the central carbon atom in the phthalide of 9-ethylcarbazole is at the 3-position in each of the carbazole nuclei (Copisarow and Weizmann, T., 1915, **107**, 878), it may reasonably be assumed that in the tricarbazylmethane colouring matters the methane carbon atom is linked to each carbazole nucleus at the *p*-position with respect to the nitrogen atom.

The constitutional formulæ of carbazole-blue and carbazole-violet are therefore represented by formulæ I and II respectively.*



(I.)



(II.)

The *chloride* of tri-3-carbazylcarbinol (III) is obtained by condensing carbazole with chloropicrin, and that of tri-9-ethyltri-3-carbazylcarbinol (IV) by condensing 9-ethylcarbazole with carbon tetrachloride.

An important property of both carbazole-blue and carbazole-violet is the ease with which they are sulphonated. This indicates that the presence of a phenylene group, like that of the benzyl and phenyl groups, makes possible the production of soluble dyes of the triphenylmethane series.

In connexion with the mechanism of formation of carbazole-blue, *N*-oxalylcarbazole cannot be regarded as an intermediate compound in the synthesis of carbazole-blue, and obviously not in the case of carbazole-violet (Copisarow, T., 1918, **113**, 816). Carbazole condenses in this case, not with oxalic acid itself, but with its decom-

* $(C_{12}H_7NR)_2C{:}C_{12}H_7NR{\cdot}OH$ is regarded as the base, whilst the carbinol, $(C_{12}H_7NR)_3C{\cdot}OH$, may be taken as the pseudo-base.

position products, formic acid and carbon monoxide. This synthesis of carbazole-blue and carbazole-violet may thus be regarded as a combination of the "aldehyde" and "phosgene" processes of formation of members of the triphenylmethane series. The formation of carbazole-blue and carbazole-violet throws interesting light on the manner of decomposition of oxalic acid, definitely indicating formic acid as an intermediate product.

The direct decomposition of oxalic acid without means of retaining the intermediate products results in the formation of carbon monoxide, carbon dioxide, and water (Calcagni, *Gazzetta*, 1920, **50**, i, 245).

Experimental.

Carbazole-blue (I).

Carbazole-blue was prepared according to Suida's method (*loc. cit.*), but the yield did not exceed 5 per cent. of the theoretical. The employment of anhydrous oxalic acid, zinc chloride, aluminium chloride, or modifying the conditions of heating gave no better results.

No carbazole-blue was formed on condensing carbazole with carbon tetrachloride in the presence of aluminium chloride.

The isolation and purification of the carbazole-blue was carried out in the following manner. The greenish-blue product of fusion of carbazole with oxalic acid was extracted with hot water until free from oxalic acid. The residue was dried, finely powdered, and exhaustively extracted with benzene in a Soxhlet apparatus. The blue product, remaining as a residue insoluble in benzene, was then extracted with alcohol, in which it is fairly soluble, the blue alcoholic solution being allowed to evaporate slowly.

In this manner, carbazole-blue was obtained as a deep blue, granular powder, exhibiting a metallic lustre on trituration, or in thin layers. It charred without melting at above 300°. Alcoholic or aqueous extracts of carbazole-blue gave no precipitate with silver nitrate or calcium chloride. The benzene extract was found to contain, in addition to unchanged carbazole, a little tri-3-carbazylmethane, as indicated by oxidation, which gave the salt of the carbinol.

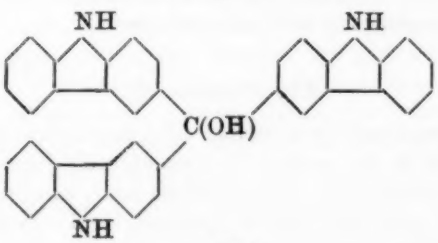
Fission of Carbazole-blue.

Bamberger and Müller (*loc. cit.*) noticed an odour of carbazole on destructive distillation of carbazole-blue alone or with zinc dust. The fact that no carbazole was actually isolated, and that destructive distillation is apt to lead, not only to fission, but also reduc-

tion (Copisarow, P., 1914, **30**, 111), made it necessary to investigate the matter further.

Pure carbazole-blue was mixed with five times its weight of powdered potassium hydroxide, and the fused mixture kept at 240—250° for half an hour. The product was extracted with hot water, filtered, washed with dilute hydrochloric acid, and dried. The dried residue was extracted with benzene, the extract being decolorised with animal charcoal and allowed to evaporate gradually. The small, grey crystals obtained in this way were recrystallised from alcohol, separating in white, pearly scales melting at 238°, and were identified as carbazole.

Tri-3-carbazylcarbinol,



(III.)

The method adopted for the synthesis of the carbinol was that employed by Baeyer and Villiger (*Ber.*, 1904, **37**, 2873) for the preparation of the carbinol of rosaniline-blue. Carbazole-blue was dissolved in pyridine with the addition of a little benzoic acid, and water gradually added until the solution became slightly turbid. The liquid was allowed to remain until its brown colour had practically disappeared, then poured into dilute sodium hydroxide, and the mixture extracted with ether.

The ethereal solution was washed several times with water, dried over sodium sulphate, the ether evaporated, and the residue crystallised twice from toluene. In this manner, the carbinol was obtained in small, white, prismatic crystals melting at 117—118°. For analysis, the substance was dried at 105° in a current of hydrogen (Found: C=83·1; H=4·64; N=7·9. $C_{37}H_{25}ON_3$ requires C=84·22; H=4·78; N=7·97 per cent.).

On adding organic or mineral acids to the carbinol or its solution, coloured salts are instantly formed. The colour of the salts varies with the acid, the range of colours being between violet and purple, the acetate being bluish-violet, the oxalate greenish-blue, the sulphate blue, and the nitrate reddish-blue to purple.

The Chloride, $(C_{12}H_8N)_2C{:}C_{12}H_8NCl$.

Carbazole-blue was dissolved in pyridine with the addition of a little benzoic acid. To the boiling solution, a saturated solution of hydrogen chloride in pyridine was gradually added with stirring. The cooled mixture was poured into dilute hydrochloric acid, filtered, washed with dilute hydrochloric acid and water, pressed, and dried. The fine, blue, granular product was purified by means of alcohol in a manner identical to that adopted in the case of carbazole-blue (Found: C = 80·46; H = 4·3; Cl = 6·4. $C_{37}H_{24}N_3Cl$ requires C = 81·36; H = 4·44; Cl = 6·5 per cent.).

This compound decomposes without melting on heating above 300°.

It is practically insoluble in water or benzene, and fairly soluble in alcohol, glacial acetic acid, or pyridine.

The Formate (I).

This was prepared by treating tri-3-carbazylcarbinol, dissolved in pyridine, with an excess of concentrated formic acid. The mixture was poured into dilute formic acid, filtered, washed with dilute formic acid and water, pressed, and dried. The blue, granular powder was purified by crystallisation from alcohol (Found: C = 81·84; H = 4·5; N = 7·48. $C_{38}H_{25}O_2N_3$ requires C = 82·1; H = 4·54; N = 7·56 per cent.).

The analytical data and general characteristics of this substance are identical with those of carbazole-blue, as indicated by Suida (*loc. cit.*) and Bamberger and Müller (*loc. cit.*).

Tri-3-carbazylmethane, $(C_{12}H_8N)_3CH$.

The reduction of carbazole-blue was carried out as described by Bamberger and Müller (*loc. cit.*). The product crystallised from ether in small, white, rhombic needles melting at 217—218°. For analysis, the substance was dried at 120° in a current of hydrogen (Found: C = 85·62; H = 4·7; N = 8·2. $C_{37}H_{25}N_3$ requires C = 86·85; H = 4·93; N = 8·22 per cent.).

Tri-3-carbazylmethane gave the corresponding coloured salts of the carbinol on oxidation with potassium permanganate in acid solution or with chloranil in the presence of acetic acid.

The Chloride and Tri-3-carbazylmethane.

These two substances were also prepared in the following manner. A suspension of carbazole in an excess of chloropicrin was heated

under an air condenser in an oil-bath for six hours, the temperature being gradually raised from 125° to 145°. The reaction is sluggish and incomplete, about 90 per cent. of the carbazole remaining unchanged. The gases evolved during the reaction contain nitrogen, carbonyl chloride, hydrogen chloride, etc. The mixture was treated with dilute hydrochloric acid and distilled in a current of steam. The residue was collected, washed with water, dried, and then extracted with benzene in a Soxhlet apparatus. The residue, a blue, granular powder, was crystallised from alcohol, and was found to consist of the chloride of tri-3-carbazylcarbinol.

The benzene extract, freed from solvent, was crystallised from ethyl alcohol, the solution being decolorised with animal charcoal. The white, crystalline product contained, in addition to unchanged carbazole, some other substance, which, owing to its small amount, could not be isolated. When this white product was oxidised with potassium permanganate in the presence of hydrochloric acid, a blue product was obtained, which, on extraction with benzene, was found to consist of carbazole and a blue powder, identified as the chloride. This clearly indicated that the white substance accompanying the unchanged carbazole was tri-3-carbazylmethane, which is formed as a by-product during the condensation.

It is to be noted that, whilst the products of condensation of carbazole with chloropicrin are identical in composition and general properties with the chloride of tri-3-carbazylcarbinol and tri-3-carbazylmethane, the colouring matter appears to be somewhat duller and redder. This is probably due to the presence of traces of the chloride of benzhydrol, $R_2CH{\cdot}OH$, formed during the condensation and oxidation.

Carbazole-violet (II).

9-Ethylcarbazole was fused with ten times its weight of crystallised oxalic acid, as in the case of carbazole-blue. The product was thoroughly extracted with hot water, the residue dried, and extracted with benzene in a Soxhlet apparatus. The residue, purified by crystallisation from alcohol, was a fine, violet powder exhibiting a metallic lustre on trituration or in thin layers. This product, which it is proposed to term "carbazole-violet," closely resembles carbazole-blue in its general properties. It is practically insoluble in water or benzene, and fairly soluble in alcohol or glacial acetic acid. Concentrated sulphuric acid sulphonates the substance in the cold, the mixture giving, when poured in water, a bluish-violet solution. On heating, it chars without melting (Found: C = 81·78; H = 5·4; N = 6·4. $C_{44}H_{37}O_2N_3$ requires

C=82·59; H=5·83; N=6·57 per cent.). As in the case of carbazole-blue, a small amount of the reduction product was found in the benzene extract, along with unchanged 9-ethylcarbazole.

Tri-9-ethyltri-3-carbazylmethane, $(C_{14}H_{12}N)_3CH$.

This is obtained by reducing carbazole-violet, as in the case of carbazole-blue; it crystallises from ether and benzene in white, short needles melting at 186—187°. For analysis, the substance was dried at 120° in a current of hydrogen (Found: C=85·84; H=5·9; N=6·98. $C_{43}H_{37}N_3$ requires C=86·68; H=6·26; N=7·05 per cent.).

On oxidation, as in the case of tri-3-carbazylmethane, the colour is regenerated, with the formation of the salts of the carbinol.

The Chloride, $(C_{14}H_{12}N)_2C{:}C_{14}H_{12}NCl$.

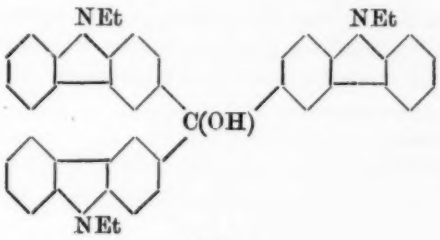
To a mixture of 55 grams (2 mols.) of 9-ethylcarbazole and 24 grams (1 mol.) of carbon tetrachloride in 400 c.c. of carbon disulphide, 40 grams of finely powdered aluminium chloride were gradually added in the course of an hour, and the reaction was completed by heating the mixture on a water-bath for eight hours. The solvent was then distilled off, the residue treated with ice and a little hydrochloric acid, and the mixture distilled in a current of steam. The residue was collected, dried, and extracted thoroughly with benzene. The portion insoluble in benzene was a violet powder of a delicate shade showing a coppery lustre in thin layers or on grinding. In its general characteristics, this substance differs but little from carbazole-blue or carbazole-violet. For analysis, it was purified by recrystallising from alcohol (Found: C=81·12; H=5·6; Cl=5·56. $C_{43}H_{36}N_3Cl$ requires C=81·93; H=5·76; Cl=5·64 per cent.).

The yield of the chloride was 87 per cent. of the theoretical, calculated on the basis of the 9-ethylcarbazole employed. Reduction in the manner adopted in the case of carbazole-blue and carbazole-violet furnished tri-9-ethyltri-3-carbazylmethane (m. p. 187°) in a much purer state than when obtained by reducing carbazole-violet.

The condensation of 9-ethylcarbazole with chloroform in the presence of aluminium chloride, in a manner similar to that employed in the condensation with carbon tetrachloride, gave, as main product, tri-9-ethyltri-3-carbazylmethane. No substance of the diphenylmethane type could be isolated. The presence of some by-product, probably of the $R_2{:}CH_2$ type, was, however, indicated

by the shades of the coloured products of oxidation. Oxidation of the twice recrystallised tri-9-ethyltri-3-carbazylmethane gave, in the presence of hydrochloric acid, a violet substance, the shade of which closely resembles that of carbazole-violet and the product of the condensation of 9-ethylcarbazole with carbon tetrachloride. Oxidation of the crude product gave, on the contrary, a deep greenish-blue substance, apparently due to the presence of the chloride of a benzhydrol.

Tri-9-ethyltri-3-carbazylcarbinol,



(IV.)

The method adopted for the preparation of this carbinol from the chloride was identical with that employed in the case of tri-3-carbazylcarbinol. After crystallisation from ether and then benzene, *tri-9-ethyltri-3-carbazylcarbinol* was obtained in small, white needles melting at 92—93°. For analysis, the substance was kept for three days under diminished pressure over paraffin, and then in a current of hydrogen at 85° (Found: C = 83·8; H = 6·0; N = 6·84. $C_{43}H_{37}ON_3$ requires C = 84·41; H = 6·1; N = 6·87 per cent.).

The general behaviour of the carbinol towards solvents and acids is similar to that exhibited by tri-3-carbazylcarbinol.

The Formate (II).

The formate was prepared by shaking a solution of tri-9-ethyltri-3-carbazylcarbinol in benzene with an excess of formic acid. The fine, violet powder which separated was collected and dried.

The analysis and general properties of this substance indicated it to be identical with carbazole-violet.

Conversion of Carbazole-violet into Carbazole-blue.

Tri-9-ethyltri-3-carbazylmethane was heated with four times its weight of hydriodic acid (b. p. 126—127°) and a little aluminium

amalgam, the temperature of the mixture being gradually raised to 130° in the course of two hours. When all the ethyl iodide was expelled (accelerated by a current of air), the residue was washed with dilute sodium carbonate and water.

The dried residue was extracted with toluene, from the decolorised solution of which small, white crystals melting at 217° separated, and were identified as tri-3-carbazylmethane. On oxidation in the presence of acid, the coloured salts of the carbinol were obtained.

The author wishes to express his thanks to Drs. C. Weizmann and H. Stephen for the interest taken in this investigation, and to acknowledge with thanks a grant from the Research Fund of the Chemical Society, covering part of the expenses.

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CLXXI.—*The Cyanine Dyes. Part III. The Constitution of Pinacyanol.*

By WILLIAM HOBSON MILLS and FRANCES MARY HAMER.

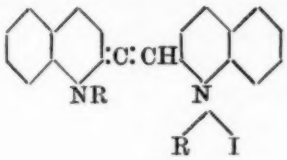
ONE of the most valuable of the photographic sensitisers in common use is a substance patented in 1905 by the Farbwerke vorm. Meister, Lucius & Brüning (Brit. Pat. 16227 of 1905; D.R.-P. 172118), and sold under the name of pinacyanol.

The action of alkali on a hot alcoholic solution of a mixture of a quinoline and a quinaldine alkyl haloid brings about, as is well known, the development of an intense reddish-purple colour, on account of the formation of an *iso*cyanine. If, however, formaldehyde, as well as alkali, is added to the solution, the colour produced is a beautiful deep blue, and the substance to which this is due is a dye of the type of pinacyanol. Corresponding with the difference in colour, these blue dyes sensitise much further into the red than the *iso*cyanines. A large number of compounds of this class have been prepared and examined in this laboratory, and the name carbocyanine has been proposed for them to provide a basis for their systematic nomenclature (Pope and Mills, *Phot. J.*, 1920, **60**, 253).

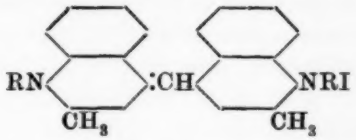
In view of the practical importance of these dyes, and of the interest attaching to the relationship between photo-sensitising

activity and structure, a definite knowledge of their constitution is much to be desired. Two structural formulæ have previously been put forward, but neither of them can be regarded as free from objection.

O. Fischer (*J. pr. Chem.*, 1918, [ii], **98**, 204) has proposed formula I, and Wise, Adam, Stewart, and Lund (*J. Ind. Eng. Chem.*, 1919, **11**, 460) suggest the constitution II.



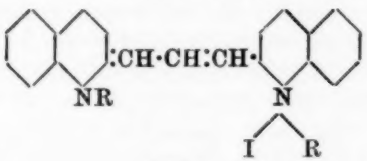
(I.)



(II.)

Fischer's formula appears not to represent the composition of the dyes correctly. It contains one atom of carbon less than is indicated by our analytical results. It is also improbable that compounds of this structure would possess the intense colour of the carbocyanines.

The formula suggested by the American investigators represents the carbocyanines as dimethyl derivatives of the true cyanines. This does not accord with their photo-sensitising action, nor does it agree with their behaviour on oxidation. The formula which our experiments have led us to regard as the most probable representation of the structure of the carbocyanines is III. It is based



(III.)

on the following facts and considerations.

(1) The carbocyanines are quaternary ammonium salts evidently containing two atoms of nitrogen and one equivalent of acid radicle in the molecule. A series of careful halogen determinations made on the dye obtained by treating quinaldine ethiodide with formaldehyde and sodium hydroxide (1:1′-diethylcarbocyanine iodide), and on the corresponding bromide, showed that the molecular weight of the iodide was 479±1.

Two molecules of quinaldine ethiodide are clearly concerned in the production of one molecule of the dye, but, since it contains carbon, hydrogen, nitrogen, and iodine only, the maximum molecular weight it could possess if derived from two molecules of

quinaldine ethiodide, with the loss of hydrogen iodide, would be 470. The observed molecular weight therefore shows that, contrary to the view of O. Fischer (*loc. cit.*), it must contain the residue of one molecule of formaldehyde.

Simple condensation with one molecule of formaldehyde would result in the addition of 12 units to the molecular weight. The observed increase of about 10 units indicates that, in addition to the elimination of hydrogen iodide and water, hydrogen (probably 2 atoms) has been removed by some process of oxidation.

The probable reaction for the formation of the dye is therefore

$$2C_{10}H_9N,C_2H_5X + CH_2O = C_{25}H_{25}N_2X + H_2O + HI + 2H,$$

and the formula $C_{25}H_{25}N_2X$ thus indicated is in excellent agreement with the analytical results.

(2) Whilst the *iso*cyanines are formed by condensation of one molecule of a quinoline alkyl iodide with one of a quinaldine alkyl iodide, two molecules of a quinaldine alkyl iodide are necessary for the formation of a carbocyanine; a quinoline alkyl iodide, if present, takes no direct part in the condensation.

This fact was discovered by O. Fischer (*loc. cit.*), and also strongly suspected by the American investigators. It was similarly discovered in this laboratory through observing that the compound produced by the action of alkali and formaldehyde on a mixture of the ethiodides of quinoline and quinaldine was identical with that obtained from quinaldine ethiodide alone.

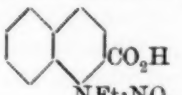
The yield is, however, very much better in the former case, and this suggested that possibly the additional amount of carbocyanine might be formed from one molecule of quinoline alkyl iodide, two molecules of formaldehyde, and one of quinaldine alkyl iodide. The action of alkali and formaldehyde on a mixture of *p*-toluquinaldine ethiodide and quinoline ethiodide was therefore investigated.

The amount of sensitiser produced was about the same as from the corresponding mixture of quinaldine ethiodide and quinoline ethiodide, and it was found to be a homogeneous substance, since, by extraction with successive quantities of methyl alcohol, it was divided into six fractions identical in properties, and analysis showed that these consisted of the 1:1′-diethyl-6:6′-dimethylcarbocyanine iodide described by Pope and Mills (*loc. cit.*). The whole of the carbocyanine formed thus contained two *p*-toluquinaldine residues, and the quinoline ethiodide did not contribute to the carbon skeleton of any portion of the dye produced. The behaviour of many other substituted quinaldine alkyl iodides in the carbocyanine condensation has been examined in this laboratory with similar results (Pope and Mills, *loc. cit.*); thus, for

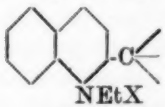
example, from bromoquinaldine ethiodide and quinoline ethiodide, a dibromocarbocyanine iodide is formed.

It therefore appears that the alkyl iodides of the quinoline bases can only take part in the carbocyanine condensation provided they contain a 2-methyl group, and in this condensation two molecules of such an alkyl iodide and one of formaldehyde are concerned.

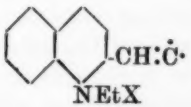
(3) When a solution of diethylcarbocyanine bromide in dilute nitric acid is heated, the dye is rapidly oxidised, and the liquid, after becoming almost immediately bright orange-red, is gradually decolorised, the colour practically disappearing after about an hour's boiling. From the residue left after the nitric acid has been evaporated, which consists of a mixture of highly soluble substances, a crystalline quaternary nitrate can be isolated. The composition of this nitrate, together with its properties, and the fact that it gives 1-ethyl-2-quinolone on oxidation with potassium ferricyanide, shows it to be quinaldinic acid ethyl nitrate (*A*). It is clearly derived from one of the quinaldine residues present in the pinacyanol molecule, and the yield of analytically pure material isolated varied, in four experiments, from 89 to 93 per cent. of the theoretical. The production of this compound shows that pinacyanol contains the grouping IV.



(*A*.)



(IV.)



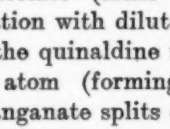
(V.)

Moreover, that it is formed so smoothly and easily further indicates that this residue is united to the rest of the molecule by an ethylenic linking, and thus that pinacyanol contains the grouping V.

The other main oxidation product, or products, are exceedingly soluble, and have not yet been identified. The residue left after the removal of the quinaldinic acid ethyl nitrate was therefore further oxidised with alkaline ferricyanide, and was found to give rise to 1-ethyl-2-quinolone.* The weight of distilled, colourless, crystalline product was 60 per cent. of the weight of ethylquinolone theoretically obtainable from one quinaldine residue in the pinacyanol originally taken. It was not quite pure (m. p. 50—54° with incipient softening at 40°; pure 1-ethyl-2-quinolone melts at 53—55·5°), but analytically pure ethylquinolone was easily isolated from it, and it was evident that far more quinolone had been produced than could possibly have been derived from the 11 per cent.

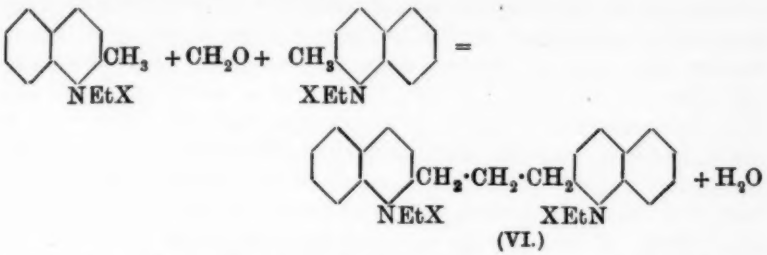
* The production of ethylquinolone by the oxidation of pinacyanol by potassium ferricyanide was observed by O. Fischer (*loc. cit.*).

of the first quinaldine residue unaccounted for as quinaldinic acid ethyl nitrate. It must therefore have been formed mainly from the second quinaldine residue present in pinacyanol. That this second quinaldine residue should be split off on oxidation as 1-ethyl-2-quinolone shows that the quinoline nucleus contained in it must be attached to the rest of the molecule through the 2-position. More precise conclusions can scarcely be drawn from this fact, for oxidation with alkaline ferricyanide is not fitted to decide more delicate points of constitution; for example, Decker and Remfry (*Ber.*, 1905, **38**, 2773) have shown that quinaldine alkyl iodides are converted by this reagent into the corresponding quinolones. The action of potassium permanganate on pinacyanol acetate in aqueous acetone solution at 0° was therefore studied (compare Mills and Wishart, this vol., p. 579). The permanganate was added gradually, and the end of the reaction was sharply marked by the persistence of the permanganate colour after a quantity corresponding with 4·8 atoms of oxygen to one molecule of pinacyanol had been added. Oxidation under these conditions brought about the fission of the pinacyanol molecule, with the production of 1-ethyl-2-quinolone. The quantity of pure substance isolated amounted to 79 per cent. of that theoretically obtainable from one quinaldine residue. The other product was exceedingly soluble and showed the behaviour of a quaternary salt. When boiled with dilute nitric acid, it gave quinaldinic acid ethyl nitrate, but the oxidation did not proceed smoothly, and the quantity of the nitrate isolated was only 25 per cent. of the theoretical yield from half the pinacyanol molecule. These observations, especially when considered in relationship to the action of potassium permanganate on dimethyl*iso*cyanine acetate (Mills and Wishart, *loc. cit.*), indicate that whilst oxidation with dilute nitric acid splits off from the pinacyanol molecule the quinaldine residue which contains the quinquevalent nitrogen atom (forming quinaldinic acid ethyl nitrate), potassium permanganate splits off, as ethylquinolone, that containing the tervalent nitrogen atom. It thus appears that the second quinaldine residue is present in pinacyanol in the form



(4) It has thus been shown that (i) the carbocyanine condensation takes place between two molecules of quinaldine alkyl iodide and one of formaldehyde, and that (ii) the two quinaldine residues are both attached to the rest of the molecule through the carbon

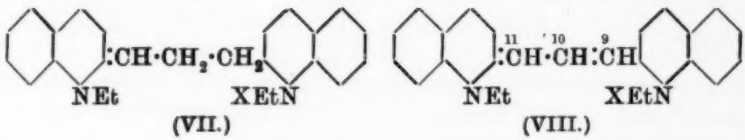
atoms of their 2-methyl groups. The main reaction concerned in the condensation must therefore be



(VI.)

This is analogous to several well-known reactions in which one molecule of formaldehyde condenses with two molecules of a compound containing a group of similar reactivity to the 2-methyl group in quinaldine ethiodide (compare Knoevenagel, *Ber.*, 1894, **27**, 2345).

In the alkaline reaction mixture, the hypothetical intermediate product, VI, would lose hydrogen iodide, forming the substance



(VII.) (VIII.)

VII, for the existence of reactions of this type is well established (compare Decker, *Ber.*, 1905, **38**, 2493).

VII is, however, not a possible formula for a substance as intensely coloured as pinacyanol. From analogy to other basic dyes, the saturated and the unsaturated nitrogen atoms in this compound must be connected by a chain of conjugated unsaturated linkings. There are reasons which make the presence of an ethylenic linking between the carbon atoms 9 and 10 exceedingly probable, and therefore we assign to pinacyanol the formula VIII. These reasons are, first, that in the closely related *iso*cyanine condensation a similar oxidation, involving the removal of two hydrogen atoms, occurs,* and, secondly, as has already been pointed out, that the great readiness with which pinacyanol can be oxidised

* The two hydrogen atoms by which formula VII differs from VIII would be unusually reactive on account of their respective positions relative to unsaturated linkings, and would therefore be readily removable. That the carbocyanine condensation involves a process of oxidation would also explain why a larger yield of sensitiser can be obtained from a given quantity of quinaldine ethiodide when the condensation is carried out in presence of quinoline ethiodide; the latter probably gives rise to substances which serve to take up this hydrogen.

to quinaldinic acid ethyl nitrate is scarcely to be accounted for unless an ethylenic linking is present in this position.

There is a somewhat remarkable reaction of pinacyanol, which is probably dependent on the presence of this unsaturated three-carbon chain uniting the two quinoline residues. If a solution of the nitrate of the dye in dilute nitric acid is carefully warmed to 60°, the orange-red colour, to which reference has already been made, suddenly appears, and, on cooling the solution, a bright red compound crystallises. This is a quaternary nitrate, and analysis indicates that it is formed by the entrance, either by substitution or addition, of two nitro-groups into the pinacyanol molecule.

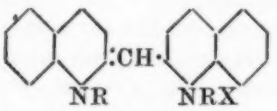
Since on oxidation it gives, like pinacyanol itself, quinaldinic acid ethyl nitrate and 1-ethyl-2-quinolone, both nitro-groups must be attached to the 3-carbon chain connecting the two quinoline residues, unless, as is less probable, one of them is in the 2′-position. This reaction, which does not take place in the presence of carbamide, accordingly recalls the action of nitrogen peroxide on quinoline-yellow (Eibner and Lange, *Annalen*, 1901, **315**, 342),

$$\begin{matrix}C_6H_4\\CO_2\end{matrix}\!\!>\!C{:}CH\cdot C_9H_6N + 2NO_2 = \begin{matrix}C_6H_4\\CO_2\end{matrix}\!\!>\!C(NO_2)\cdot CH(NO_2)\cdot C_9H_6N$$

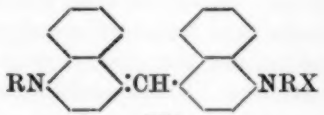
and the stability of this pinacyanol derivative, in comparison with Eibner and Lange's additive compound, would indicate that it is a substitution derivative.

(5) According to this view of the constitution of the carbocyanines, they stand in an interesting relationship to the cyanines.

The cyanines can be regarded as consisting of a 1-alkylquinolenyl radicle united through the methenyl group :CH· to a univalent residue of an alkylquinolinium salt. Since the union can take place from a 2- to a 2′-position, a 4- to a 4′-position, or from a 2- to a 4′-position, there are three types of cyanines:



(I.)



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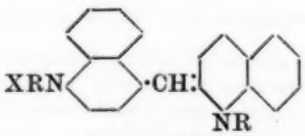
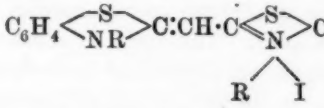


(III.)

The dyes of type II are the true cyanines, those of type III are the *iso*cyanines. Dyes of type I are at present unknown in the

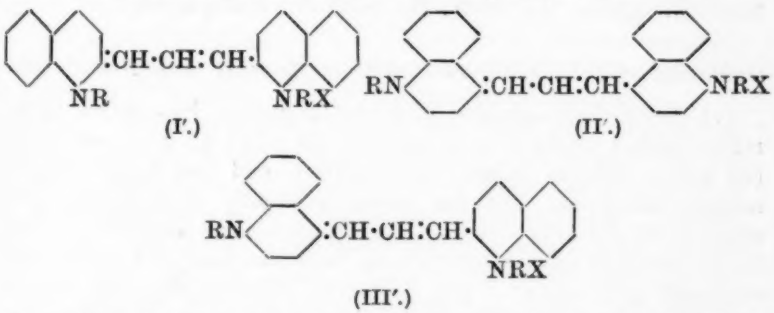
quinoline series, but the compounds obtained by Hofmann (*Ber.*, 1887, **20**, 2262) by the action of ammonia on a mixture of the alkyl iodides of benzothiazole and 1-methylbenzothiazole are so closely analogous to the *iso*cyanines in the method by which they are formed and in their properties that they undoubtedly possess the constitution



and thus are representatives of this class.

According to the constitution now assigned to the carbocyanines, they are cyanines of class I, in which the carbon chain connecting the two quinoline nuclei has been lengthened by the introduction of the group ·CH:CH·. The great resemblance between the carbocyanine and the cyanine dyes thus finds a simple explanation, and the deeper colour of the carbocyanines, compared with the reddish-purple of the cyanines of the benzothiazole series, is associated with the lengthening of the chain of conjugated unsaturated linkings which connects the two nitrogen atoms.

Corresponding with the three types of cyanines, the following three classes of carbocyanines should be capable of existence:



(I′.) (II′.)

(III′.)

Thus, in addition to the dyes of the type of pinacyanol (I′), it should be possible to prepare compounds of the formulæ II′ and III′, which would probably prove to be dyes possessing powerful photo-sensitising properties similar to those shown by the rest of this group of compounds.

Experimental.

Composition of 1:1′-*Diethylcarbocyanine Salts.*

1:1′-Diethylcarbocyanine iodide, prepared, as described by Pope and Mills (*loc. cit.*), by the action of formaldehyde and alkali on

a mixture of quinaldine ethiodide and quinoline ethiodide, after having been crystallised five times from methyl alcohol and dried to constant weight at 145°/20—30 mm., was found, on analysis by the Carius method, to contain I = 26·60 per cent. The iodide prepared from quinaldine ethiodide alone was found in two analyses to contain I = 26·61 and 26·68 per cent. The iodide prepared from quinaldine ethiodide and quinoline methiodide gave I = 26·53 and 26·54 per cent. The mean of these values, which are probably slightly too high, on account of occlusion of silver nitrate by the silver iodide, is 26·59* ($C_{25}H_{25}N_2I$ requires I = 26·43; Fischer's formula, $C_{24}H_{23}N_2I$ requires I = 27·23 per cent.).

1 : 1′-Diethylcarbocyanine bromide, after drying to constant weight at 140°/20—30 mm., was found to contain Br = 18·49 and 18·53 per cent. in two experiments carried out by Mr. J. E. G. Harris. These analyses, to which, on account of the accuracy of the Carius method for the estimation of bromine, we attach especial importance, give a molecular weight of 432 for the bromide (corresponding with a molecular weight of 479 for the iodide) ($C_{25}H_{25}N_2Br$ requires Br = 18·45; Fischer's formula, $C_{24}H_{23}N_2Br$ requires Br = 19·06 per cent.).

Combustion of the dried bromide gave results in excellent agreement with the formula $C_{25}H_{25}N_2Br$ (Found: C = 69·18; H = 5·83; N = 6·55. Calc.: C = 69·26; H = 5·82; N = 6·47 per cent.).

Oxidation of 1 : 1′-Diethylcarbocyanine Bromide with Nitric Acid.

1 : 1′-Diethylcarbocyanine bromide (2 grams) was boiled under reflux with a mixture of nitric acid (D 1·42; 40 c.c.) and water (40 c.c.). Nitrous fumes were evolved, and the liquid rapidly became orange-red, but the colour gradually disappeared, and, after about one hour's boiling, the liquid became colourless.† The liquid was then evaporated, first on the water-bath and finally over sulphuric acid under 2 mm. pressure. The residue was treated with water, and a small quantity (about 0·1 gram) of undissolved material was removed by extraction with chloroform. The aqueous layer was again evaporated on the water-bath, and finally in a highly exhausted desiccator over sulphuric acid. The residue gradually solidified, and, by trituration with a little acetone, an almost colourless, crystalline solid was readily isolated. After

* These analyses were carried out by one of us and Mr. F. H. Jeffery.

† During this operation a small quantity of a heavy volatile oil with a pungent odour resembling that of chloropicrin appeared in the condenser. The amounts obtained were insufficient to enable the substance to be identified, but it contained nitrogen and bromine and was possibly bromonitromethane.

recrystallisation from absolute alcohol, it melted and decomposed at 109°.

The following observations show that this compound is quinaldinic acid ethyl nitrate:

(i) It is a nitrate. An estimation of the NO_3 radicle by "nitron" gave $NO_3=23{\cdot}6$. $C_{12}H_{12}O_2N{\cdot}NO_3$ requires $NO_3=23{\cdot}5$ per cent. (Found: $N=10{\cdot}8$. $C_{12}H_{12}O_5N_2$ requires $N=10{\cdot}6$ per cent.).

(ii) Although a quaternary ethyl nitrate (as shown by its conversion into ethylquinolone on oxidation and its behaviour with excess of alkali), it was strongly acid, and could be sharply titrated with alkali and phenolphthalein, and therefore contained a carboxyl group (Found: $CO_2H=17{\cdot}05$. $C_{11}H_{11}O_3N_2{\cdot}CO_2H$ requires $CO_2H=17{\cdot}04$ per cent.).

(iii) Its conversion by alkaline ferricyanide into ethyl-2-quinolone shows that the carboxyl group was in the 2-position. An aqueous solution of the nitrate (0·5 gram) was slowly dropped into a solution of potassium ferricyanide (6 grams) in 5 per cent. sodium hydroxide (60 c.c.) maintained at 0—5°. The resulting liquid was extracted with ether, and the residue left on evaporation of the ether, after drying with potassium hydroxide, was pure 1-ethyl-2-quinolone. Its melting point, 53—55·5°, was identical with that of a specimen of ethylquinolone, prepared for comparison by oxidising quinoline ethiodide, and a mixture of the two specimens melted at the same temperature. The weight of quinolone obtained was 0·27 gram, or 82 per cent. of the theoretical amount.

The material from which the quinaldinic acid ethyl nitrate had been separated by means of acetone was then examined. It was left, after evaporation of the acetone, as a clean, brown oil, which was excessively soluble in water, alcohol, or acetone. It was investigated in various ways, such as by crystallisation of the platinichloride, without much further information being gained. It was therefore oxidised with alkaline potassium ferricyanide. The material obtained from 2 grams of diethylcarbocyanine bromide by oxidation with dilute nitric acid, and subsequent removal of the quinaldinic acid ethyl nitrate, was dissolved in water, a small quantity of insoluble matter being removed by filtration, and the liquid was dropped into a solution of potassium ferricyanide (8 grams) in 5 per cent. sodium hydroxide solution at 0—5°. The quinolone produced was extracted with ether and dried with potassium hydroxide.

The material from three such experiments was united and distilled under 2 mm. pressure from an oil-bath at 155—168°. The distillate was a colourless oil, which solidified to crystals melting

at 50—54°, with previous softening at 40°. It was therefore not quite pure, and was recrystallised from light petroleum. It then melted at 50—54·5°, and was shown by its general characters and analysis to be 1-ethyl-2-quinolone (Found: N = 8·3. Calc.: N = 8·1 per cent.).

The quantities obtained in these experiments were as follows. By the oxidation of 6 grams of 1:1′-diethylcarbocyanine bromide, $C_{25}H_{25}N_2Br,CH_3OH$, 3·03 grams of quinaldinic acid ethyl nitrate were obtained. This melted at 107—108°, and was pure (Found: CO_2H = 17·2; NO_3 = 23·6. Calc.: CO_2H = 17·04; NO_3 = 23·5 per cent.). This weight is 89 per cent. of that theoretically obtainable.

The weight of crude 1-ethyl-2-quinolone obtained was 1·64 grams. The weight of redistilled material was 1·35 grams, which is 60 per cent. of the weight of quinolone theoretically obtainable from one quinaldine nucleus in the pinacyanol taken. The weight of recrystallised material from which the sample for analysis was taken was 0·76 gram.

Oxidation of 1:1′*-Diethylcarbocyanine Acetate with Potassium Permanganate.*

To prepare the acetate, a solution of 1:1′-diethylcarbocyanine bromide (4 grams) in boiling rectified spirit (450 c.c.) was treated with a hot saturated aqueous solution of silver acetate (1·44 grams). The residue obtained after evaporating the filtrate from the precipitated silver bromide was dissolved in a mixture of acetone (450 c.c.) and water (450 c.c.). Into this solution, which was mechanically stirred and kept at 0—5°, 140 c.c. of a solution of potassium permanganate containing 3·16 grams per litre were slowly dropped, an end-point having been reached when 137 c.c. had been added. The red filtrate, which was neutral to litmus, was extracted with ether after evaporating the acetone under diminished pressure. The brown, ethereal extract was shaken with very dilute hydrochloric acid, which extracted some tarry matter (0·18 gram), leaving an almost colourless solution. This was dried with potassium hydroxide and then evaporated; the residue (1·26 grams), which soon crystallised, melted at 45—50°. When distilled under diminished pressure, this gave a colourless distillate of pure 1-ethyl-2-quinolone (melting point, 52—55°; melting point of a mixture with pure 1-ethyl-2-quinolone, 52—55°) (Found: C = 76·1; H = 6·7. Calc.: C = 76·3; H = 6·4 per cent.). The weight of the distillate was 1·18 grams, which is 79 per cent. of the theoretical yield.

The aqueous solution left after extraction of the ethylquinolone

was acidified with hydrochloric acid, evaporated, and the residue then treated with absolute alcohol to separate the organic matter from potassium chloride.

The brown material left after evaporation of the alcohol was boiled for thirty hours with 140 c.c. of dilute nitric acid (D 1·2), and the solution was then examined in the same way as that obtained by oxidising diethylcarbocyanine bromide with nitric acid.

The weight of quinaldinic acid ethyl nitrate obtained was 0·61 gram, or 27 per cent. of the theoretical amount, and further oxidation of the residual material with alkaline ferricyanide gave 0·46 gram of ethylquinolone, equivalent to 31 per cent. of the theoretical yield from the original diethylcarbocyanine acetate.

The Red Salts obtained by the Action of Nitric Acid on 1:1′-Diethylcarbocyanine Salts.

1:1′-Diethylcarbocyanine bromide (1 gram) was dissolved in dilute nitric acid by warming to 40° with a mixture of 4 c.c. of nitric acid (D 1·42), previously boiled to expel oxides of nitrogen, and water (16 c.c.). The bromine was then exactly precipitated with silver nitrate, and the blue or green filtrate, containing the nitrate of the dye, was warmed to 60—65°, when the liquid suddenly turned orange, and red crystals began to separate. The liquid was cooled to 0°, and the crystals were collected. By boiling the filtrate a short time and cooling to 0°, a further yield was obtained, and the process of boiling the filtrate and cooling was repeated as long as fresh quantities of crystals separated; 13 grams of 1:1′-diethylcarbocyanine bromide thus treated gave 7·36 grams of the red crystals. The yield is less if larger quantities of carbocyanine than 1 gram are taken.

The reaction is dependent on the production of oxides of nitrogen. If commercial nitric acid, not previously boiled, is employed, the colour change takes place considerably below 60°. On the other hand, if carbamide is added, the mixture can be boiled without the formation of the red salt. This red salt is a quaternary nitrate. To obtain a compound which could be more accurately analysed, it was converted into the corresponding bromide by dissolving in boiling water and adding the solution to an equal volume of a hot concentrated solution of potassium bromide. The red bromide began to crystallise from the hot solution, and separated practically completely on cooling. This treatment with potassium bromide was then repeated three times, and the product was finally recrystallised from hot water.

For analysis, it was dried at 50°/20—30 mm. The dried material melted and decomposed at 201—202° (Found: C=56·76, 56·65; H=4·80, 4·58; N=10·52, 10·73; Br=15·37, 15·37, 15·16. $C_{25}H_{23}O_4N_4Br$ requires C=57·4; H=4·42; N=10·7; Br=15·27 per cent. Loss on drying: 6·92, 7·75. $C_{25}H_{23}O_4N_4Br,2H_2O$ requires H_2O=6·9 per cent.).

Oxidation of the Red Nitrate.—One gram was boiled with a mixture of 10 c.c. of nitric acid (D 1·42) and water (10 c.c.). Oxides of nitrogen were evolved, the colour slowly faded, and, after boiling under reflux for six hours, a pale yellow liquid was obtained. This liquid was treated in the same way as the similar solution obtained by oxidising diethylcarbocyanine bromide with dilute nitric acid (p. 1558), and the same products, namely, quinaldinic acid ethyl nitrate and 1-ethyl-2-quinolone, were similarly isolated. From 4 grams of the red nitrate, corresponding with 3·95 grams of anhydrous substance, were obtained 1·51 grams of quinaldinic acid ethyl nitrate (73 per cent. of the theoretical quantity) and 0·84 gram of ethylquinolone melting at 52—53° (62 per cent. of the theoretical quantity).

Corresponding experiments were carried out with the bromide. This salt was much more rapidly attacked by the dilute nitric acid, the bromine present evidently assisting the oxidation, and the volatile, heavy oil, to which reference has already been made (p. 1558), appeared in the condenser, otherwise the products of oxidation were the same. Quinaldinic acid ethyl nitrate and 1-ethyl-2-quinolone were obtained in quantities corresponding with 93 per cent. and 60 per cent., respectively, of the theoretical amounts.

One of us (F.M.H.) is indebted to the Department of Scientific and Industrial Research for a grant, for which she desires to express her thanks.

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CLXXII.—*The Coagulation of Gold Hydrosols by Electrolytes. The Change in Colour, Influence of Temperature, and Reproducibility of the Hydrosol.*

By Jñanendra Nath Mukherjee and Basil Constantine Papaconstantinou.

In view of the results obtained by one of us (this vol., p. 350) with arsenious sulphide, it was thought desirable to investigate the influence of temperature on the precipitation of gold sols. In the course of this work it was found necessary to examine the reproducibility of the sols prepared by Zsigmondy's nucleus method. A spectrophotometric study of the changes in colour on coagulation has been made, and this has been utilised to measure the rate of precipitation.

Preparation of the Hydrosol.

All the sols were prepared by Zsigmondy's nucleus method. The specific conductivity of the water obtained from a pure tin condenser varied from 2×10^{-6} to 3×10^{-6} mhos. at 15°.

The nucleus solution was prepared as follows:

To 100 c.c. of pure water in a resistance-glass beaker were added 2 c.c. of a solution of chloroauric acid containing 6 grams of the acid in a litre, followed by 6 c.c. of a $N/18$-solution of pure potassium carbonate. Five c.c. of a saturated solution of phosphorus in ether were diluted to 100 c.c. with pure ether, and the solution was added to the gold solution gradually—a few drops at a time. After each addition the solution was stirred, and this was continued until a deep chocolate colour was produced. It was then heated, and a "red" sol resulted.

To prepare the hydrosol proper, 2 c.c. of the chloroauric acid solution were added to 100 c.c. of water, followed by 6 c.c. of the potassium carbonate solution. The mixture was then heated to boiling, and 4 c.c. of the nucleus sol were added, followed by 4—5 c.c. of a 0·03 per cent. solution of formaldehyde. The ruby-red sol which was formed was boiled for a minute.

The hydrosols obtained in this way have all the properties of the best solutions prepared by Zsigmondy. In the cardioid ultramicroscope, the hydrosols show mostly green particles with a few brown ones. The sols contain 0·067 gram of gold per litre.

The Colour Changes in a Gold Hydrosol on the Addition of an Electrolyte.

Zsigmondy (*Annalen*, 1898, **301**, 46) studied the colour changes qualitatively only. In the numerous subsequent researches on the optical properties of gold sols, the change in the absorption on coagulation has not been examined.

The changes in colour were observed with a König-Martens spectrophotometer. The changes in the colour from red to blue on the addition of an electrolyte are mainly a result of a change in the absorption-coefficient of red and violet rays. The change is greatest in the red region. There is a limiting value of the absorption-coefficient corresponding with the blue colour of the sol, and these limiting values are independent of the nature of the electrolytes used. The coefficients were calculated from the equation

$$K = K_1/2{\cdot}306 = \frac{1}{d}\log_{10}\frac{\tan^2 a}{\tan^2 a_0}\,*$$

(Hildebrand, *Zeitsch. Elektrochem.*, 1908, **14**, 349).

In studying the precipitation, equal volumes of sol and electrolyte were mixed. The coefficients for the pure sol refer to that for the sol diluted with an equal volume of pure water. The electrolytes used were potassium chloride, sodium chloride, barium chloride, potassium nitrate, strontium nitrate, and potassium sulphate.

The results are given in Fig. 1, and are the mean of observations with different samples of sols and different electrolytes. The wave-lengths are correct within $\pm 1\,\mu\mu$. It is interesting to note that in the region near $523\,\mu\mu$ there is scarcely any change in the absorption-coefficient.

It will be seen later that the results obtained for the absorption of light by the hydrosols, prepared under exactly similar conditions, differ a little among themselves except in this region, which is close to the spectral region, where the absorption is at a maximum (near $506\,\mu\mu$) (compare Ehrenhaft, *Ann. Physik*, 1903, [iv], **11**, 489).

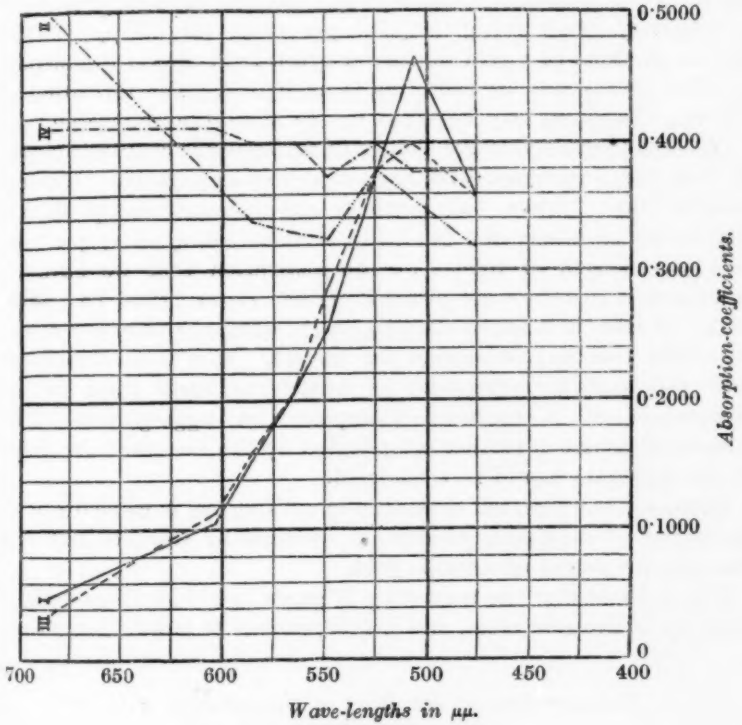
Assuming the particles in a gold sol to be spherical and that there are many particles to a wave-length of light, Garnett (*Phil. Trans.*, 1904, [*A*], **203**, 385; 1906, [*A*], **205**, 237) deduces that the maximum of absorption should be for light of wave-length $533\,\mu\mu$. Mie (*Ann. Physik*, 1908, [iv], **25**, 377) also deduces from his theory that the maximum

* a_0 = the angle for water or electrolyte solution alone.

of the pure (corrected) absorption lies in the region 525 to 550 $\mu\mu$. He further shows that for spherical particles the region of maximum of absorption does not vary with the size of the particles, although the value of the absorption-coefficient depends on the size.

According to these theories, the colour of a gold sol by trans-

FIG. 1.



I. *Hydrosol diluted with water.*
II. ,, *mixed with electrolyte.*
III. *Nucleus sol dilute with water.*
IV. *Hydrosol mixed with electrolyte.*

mitted light is the result of two properties of the gold particles or aggregates:

(1) Minute, spherical gold particles have a fairly well-defined maximum of absorption in the green. Reflection in the ordinary sense is very weak in this case, and the colour is due to the absorption of the green light, which is the colour of the light scattered most strongly by these particles.

(2) With increasing aggregation, as the size becomes comparable

to the wave-length of light there is increasing reflection. When the size becomes sufficiently large, the optical discontinuity of the medium becomes manifest as a turbidity. As is to be expected from the properties of metallic gold, red and yellow rays are mostly reflected, and the transmitted light becomes correspondingly weaker in the red and yellow.

The observed constancy of the absorption-coefficient therefore indicates two possibilities, namely: (1) The reflection of green light is relatively small for gold (47·3 per cent. for 500 $\mu\mu$). The minute particles in a gold sol scatter green light almost completely, and the part played by reflection is negligible. The formation of clusters, therefore, may be taken not to affect the absorption.

(2) It is possible that the change in scattering is counterbalanced by that due to reflection with the progress of aggregation. Garnett remarks that "when the particles are not sufficiently thickly distributed to satisfy the condition of there being many particles to a wave-length of light . . . the absorption that we have investigated is therefore not present" (*Phil. Trans.*, 1904, [*A*], **203**, 402). Indeed, it is found that, on coagulation, the intensity of the blue light (500 $\mu\mu$) diminishes for the sol. This is in accordance with the theories mentioned, as neither of them leads to the expectation of a constant absorption on aggregation. The theoretical aspect is further complicated by the fact that the shape of the aggregate has to be considered.

However, the observed constancy is striking, as it coincides with the region of maximum absorption deduced by Garnett and Mie from the properties of metallic gold.

It is possible that the scattering of green light is a characteristic property of the gold atom, and is independent of cluster formation.

The Measurement of the Rate of Coagulation with the Spectrophotometer.

The change in absorption on coagulation is great in the red region, and it has been utilised to measure the rate of precipitation at the ordinary temperature. The reciprocal of the time required to reach the limit of absorption is a measure of the rate of coagulation. As a characteristic change in the sol itself is utilised, this method has an advantage over others dependent on an arbitrarily selected stage of change. For the fine sols used in this work, the direct method of determining the rate of decrease in the number of particles is not possible with ordinary ultramicroscopes (Zsigmondy, *Zeitsch. physikal. Chem.*, 1918, **92**, 600).

This simple spectrophotometric method can be used with a suit-

able ultramicroscope with economy of labour and time. The number of particles corresponding with the absorption-coefficient values can be determined by the ultramicroscope, and their mutual relationship can be utilised to substitute the spectrophotometer for the tedious ultramicroscopic work. This is possible for the whole range of changes in colour from red to blue, but is not applicable when the limit of absorption has been reached.

The influence of the concentration of an electrolyte has been followed with the spectrophotometer for potassium chloride, potassium sulphate, potassium nitrate, and barium chloride. The mean results of three observations are given in tables I—III. The absorption-coefficients are for light of wave-length 683 $\mu\mu$. The observations show that for low concentrations of an electrolyte the "limiting" values of absorption are not reached, and coagulation practically stops at a certain stage.

TABLE I.

Electrolyte: Potassium Chloride.

Time in minutes after mixing equal volumes of electrolyte. and sol.	Absorption-coefficients for various concentrations.		
	N/24.	*N*/26.	*N*/28.
—	0·0453	0·0453	0·0453
0·5	0·3732	0·2867	0·1683
1	0·438	0·3630	0·2257
1·5	0·4497	0·4046	—
2	—	0·438	0·2777
3	—	0·4497	0·3431
5	—	—	0·3836
9	—	—	0·4263
13	—	—	0·438
15	—	—	0·4497

TABLE II.

Potassium Nitrate.

Time.	Concentration.		
	N/24.	*N*/26.	*N*/30.
—	0·0453	0·0453	0·0453
0·5	0·3336	—	—
1	0·4263	0·2866	0·269
1·5	0·4497	0·3271	0·3143
2	—	0·3629	0·3336
3	—	0·4156	0·3732
4	—	0·438	0·394
5	—	0·4497	—
8	—	—	0·4263
10	—	—	0·438
16	—	—	0·4497

TABLE III.

Barium Chloride.

Time.	Concentration. 0·852N/900.	0·852N/1000.	0·852N/1100.
—	0·0453	0·0453	0·0453
1	0·2257	—	0·1603
2	0·2867	—	0·2007
4	0·3529	—	0·2687
5	0·3836	0·3051	0·3051
7	0·438	0·3431	0·3237
8	0·4497	—	0·3336
9	0·4497	0·3836	0·3529
11	—	0·4263	0·363
13	—	0·4497	0·363
16	—	—	0·3732

These experiments were carried out within a short interval and with the same sol. There is scarcely any difference between the coagulating effects of the three potassium salts. Smoluchowski (*Zeitsch. physikal. Chem.*, 1917, **92**, 129) has deduced the following equation for the rate of decrease in the total number of particles:

$$n_t = \frac{n}{1+\frac{t}{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the total number of particles in unit volume just after mixing the sol with the electrolyte (zero time), n_t is the number at time t (second), and T is characteristic of the rate of coagulation.

Zsigmondy finds that when the minimum coagulation-time has been reached, two particles, on coming in contact as a result of their Brownian movement, are held together by forces of cohesion. The work of Westgren and Reitstötter (*Zeitsch. physikal. Chem.*, 1918, **92**, 750) lends support to this, as all these authors find that the radius of the effective sphere of attraction (as defined by Smoluchowski) is nearly equal to twice the radius of the particles. Under these conditions,

$$T = \frac{3}{4}\frac{N_0\eta}{R\theta n\epsilon} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where η = the viscosity of the solution.
R = the gas constant.
N_0 = the Avogadro number.
θ = the absolute temperature.
ϵ = the fraction of mutual collisions between the particles which result in a stable union.

For a constant value of $n_t = n'$, it is evident that

$$\epsilon . t = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or

$$\epsilon = \frac{k}{t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The reciprocal of the times for a definite change is thus directly proportional to the fraction of collisions which result in coalescence, and hence measures the rate of coagulation. The data obtained on the influence of concentration will be discussed on another occasion. The equations given above will be discussed later when dealing with the influence of temperature.

The Influence of Temperature.

The method used by one of us (*loc. cit.*) was adopted. The great variation in the colour of a ruby-red gold sol makes it suitable to use a definite shade of violet-red or bluish-violet for comparison. Standards for comparison were made by arresting the colour-change at a selected stage with gelatin, and, with care, perfectly reproducible standards can be prepared. The times necessary for the sol to change to the colour of the standard are given below.

TABLE IV.

Electrolyte: 0·852N/1000-*Barium Chloride.*

	Violet.		Blue.	
	I.	II.	I.	II.
Sol. A	6 min.	6 min.	29 min.	29 min.
Sol. B	2 min.	2 min. 25 sec.	10 min. 45 sec.	10 min. 30 sec.

The results are the mean of six observations taken separately by each of us. Sol B was obtained by boiling sol A for a few minutes and then cooling. It will be seen that the boiling produces a change in the sol.

The concentration of the electrolyte used for producing the change in the colour should be such as will bring about a slow rate of precipitation. About 2 c.c. of a 2 per cent. gelatin solution (liquid) were added to 10 c.c. of the sol–electrolyte mixture. The same standards remain satisfactory for ten to twelve days. Wide test-tubes were used to secure a suitable depth of colour. As is well known, ruby-red gold sols are extremely sensitive to impurities. Reproducible results can only be obtained if the vessels are cleaned with sufficient care. The glass vessels were washed with conductivity water after the usual cleaning with hot chromic acid and distilled water. The test-tubes were washed with boiling dis-

tilled water (after chromic acid had been used), then with conductivity water, and finally by passing steam derived from conductivity water. They were then dried in a steam-oven. There is a noticeable difference between cleaning with distilled water and conductivity water. Table V illustrates the reproducibility of the results.

TABLE V.

N/1000-*Strontium Nitrate.*

	Observations.											
	1.		2.		3.		4.		5.		6.	
Times.	Min.	Sec.	Min.	Sec.	Min.	Sec.	Min.	Sec.	Min.	Sec.	Min.	Sec.
Violet...	1	10	1	6	1	11	1	13	1	0	1	12
Blue ...	5	45	5	48	5	30	5	30	3	30	6	0

In each case, three to five readings were taken. With all these precautions, at times discordant results were obtained, which were probably due to the occasional presence of particles of dust. The agreement between the different observations and the appearance of the characteristic blue colour is the surest indication of the absence of impurities. With long intervals, it is difficult to avoid dust. A slow change in colour is also much less easily perceptible to the eye. For these reasons, it was found suitable to use concentrations of electrolytes which change the colour to blue within an hour. As different standards were used, they are indicated as V_1, V_2, etc., for violet standards, and in a similar manner for blue standards.

TABLE VI.

Electrolyte.	Standards.		Temperatures. 15°.	30°.	50°.
N/30-potassium chloride	*V*	Sol. C.	5 min.	10 min.	8 min. 30 sec.
N/30- ,, sulphate	,,	Sol. D.	30 sec.	10 sec.	10 sec.
N/30- ,, ,,	,,	,,	42 sec.	18 sec.	12 sec.

TABLE VII.

Electrolyte: Barium Chloride. Sol E.

Concentration.	Standards.	Temperatures. 15°.	30°.	40°.	50°.
0·852*N*/1000	V_2	7 min.	6 min.	4 min. 50 sec.	4 min. 20 sec.
0·852*N*/1000	B_2	34 ,,	23 ,,	—	13 min. 30 sec.
0·852*N*/1200	V_2	23 ,,	13 ,,	12 min. 30 sec.	6 min. 15 sec.
0·852*N*/1200	B_2	124 ,,	74 ,,	62 min.	—

TABLE VIII.

Electrolyte: Strontium Nitrate. Sol F.

Concentration.	Standards.	Temperature. 15°.	30°.	50°.
N/1000	V_3	1 min. 10 sec.	20 sec.	8 sec.
N/1000	B_3	8 min. 15 sec.	1 min. 40 sec.	45 sec.

With barium chloride and strontium nitrate there is a distinct increase in the rate of coagulation with rise of temperature. Potassium chloride has been examined at different concentrations. Temperature has a relatively small effect in the case of the potassium salts. With potassium chloride, both an increase and a decrease in the coagulation times have been observed with rise of temperature. This behaviour is similar to that observed by one of us in the case of arsenious sulphide sols and aluminium sulphate. The effect of temperature is also dependent on the concentration of the electrolyte.

Westgren (*Arkiv. Kem. Min. Geol.*, 1918, **7**, No. 6) has found that, in the case of coarse gold sols, sodium chloride and hydrochloric acid show an increase in the rate of precipitation with rise in temperature. With sodium hydroxide, he found no change in the rate with rise of temperature. From equations (1) and (2), if n and n' have the same values, we have

$$\frac{t\theta\epsilon}{\eta} = k, \text{ a constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $$k = \frac{3}{4}\frac{n-n'}{n.n'} \cdot \frac{N_0}{R}.$$

From equation (5), the variation in t can be calculated. If ϵ remains constant, we have

$$\frac{t\theta}{\eta} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

that is, the times are proportional to the values of $\frac{\eta}{\theta}$ at different temperatures. At 15°, 30°, 40°, and 50°, $\frac{\eta}{\theta}$ has the values $3{\cdot}96 \times 10^{-5}$, $3{\cdot}3 \times 10^{-5}$, $2{\cdot}1 \times 10^{-5}$, and $1{\cdot}7 \times 10^{-5}$ respectively.

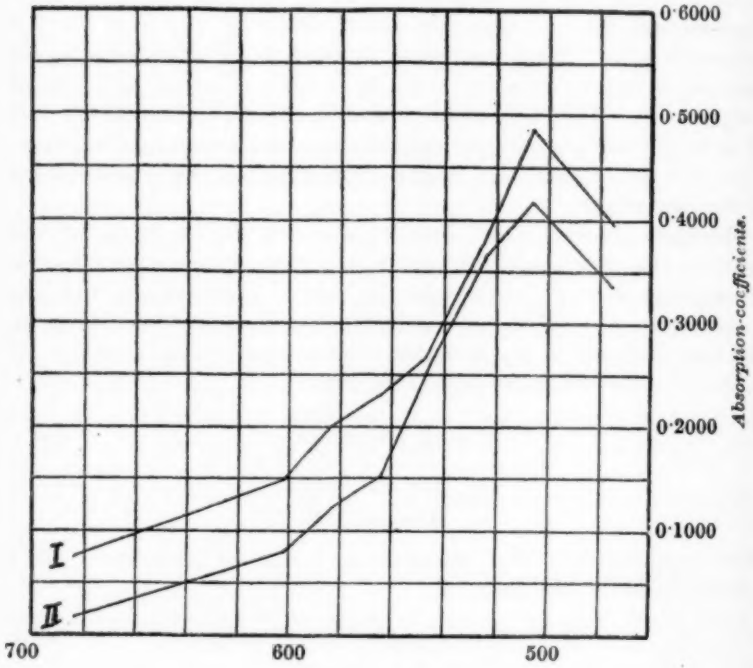
The results with hydrosols of gold and arsenious sulphide show that ϵ varies with temperature, and that the variation is determined by the nature of the electrolyte. For any given concentration of an electrolyte, ϵ measures its coagulating power. On the adsorption theory, the coagulating power of an ion is determined by its adsorbability. In order to explain the results on the

adsorption theory, it must be assumed, as pointed out previously, that the adsorbability of an ion depends on the temperature (this vol., p. 350).

The Reproducibility of the Hydrosols prepared by the Nucleus Method.

In the course of this investigation, it was noticed that these sols, even when prepared under identical conditions, do not give

FIG. 2.



I. *Upper limit of absorption.*
II. *Lower limit of absorption.*

the same coagulation times. According to Zsigmondy, the sols are reproducible if the quality of the water is unchanged. We find that the various samples of gold sols (prepared in an identical manner) show small, but perceptible, differences in coagulation times, although they have constant gold numbers. This is due to the fact that the gold numbers are independent of the slight differences in the quality of the sols.

Some twelve samples were prepared under the same conditions, and the absorption and the coagulation times were compared. The latter are extremely sensitive to any change in the sol. The limits of variation in the absorption-coefficients will be evident from Fig. 2.

It will be observed that the variation is least in the region 520 to 540 $\mu\mu$.

A sol, on keeping, undergoes somewhat irregular changes, which may in part be due to particles of dust getting in accidentally, and in part to the fungus that grows in these sols. For this reason, it is necessary to vary one factor only at a time and compare its effects. Table IX illustrates the variations, the same "violet" and "blue" standards being used. The times given are the mean of three to five observations. The last column gives the time that has passed since the preparation of the sol. The sols were kept in resistance-glass vessels. Sol I is an "old" preparation kept for two months. It was boiled twice during this interval to prevent organic growths.

TABLE IX.

Electrolyte: 0·852N/1200-*Barium Chloride.*

Standards.	Sol G. Min.	Sol G. Sec.	Sol H. Min.	Sol H. Sec.	Age.	Sol I. Min.	Sol I. S
Violet	3	15	3	35	2 days.		—
„	2	30	8	0	3 „	11	0
„	1	4	6	15	4 „	12	30
„	2	0	6	52	5 „	12	30
„	2	45	4	10	6 „	12	30
Blue	7	0	6	30	2 „		—
„	5	45	18	0	3 „	22	0
„	4	40	19	0	4 „	30	0
„	9	0	22	30	5 „	30	30
„	9	0	14	0	6 „	33	0

On the other hand, reproducible results were obtained in some instances. At the suggestion of Professor Donnan, the gold number of a number of soaps has been determined. The sols give a constant gold number for the same soap solution.

We desire to express our thanks to Professor F. G. Donnan, F.R.S., for his kind interest in this work, and also to Dr. J. C. Ghosh.

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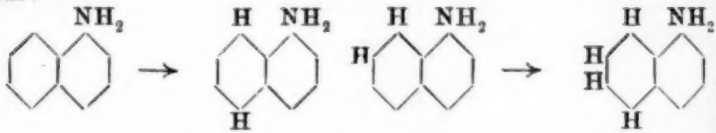
CLXXIII.—*Studies in the Dihydronaphthalene Series. Part I. The* ar-*Dihydro-α-naphthylamines and their Derivatives.*

By Frederick Maurice Rowe and Esther Levin.

The investigation of the conditions governing the conversion of α-naphthylamine into *ar*-tetrahydro-α-naphthylamine by the action of sodium and an alcohol carried out by one of us (T., 1918, **113**, 955; *J. Soc. Dyers and Col.*, 1919, **35**, 128) culminated in the proof that the first stage in the reaction is the formation of 5:8-dihydro-α-naphthylamine, which undergoes isomeric change to the 5:6- or 7:8-compound, and that the latter is then reduced to the tetrahydro-derivative (*J. Soc. Chem. Ind.*, 1920, **39**, 241T), thus:



There appears to be little doubt that the reason why *ar*-tetrahydro-α-naphthylamine has been obtained in the past only when sodium and amyl alcohol have been employed for the reduction, and not when other alcohols have been used, is that the normal conditions of the reaction have been suitable for the isomerisation of the intermediate 5:8-dihydro-α-naphthylamine only in the former case. The isomerisation, which is effected by heating with sodium alkyloxide, is influenced by both the factors of temperature and concentration of the alkali.

There is an important difference in properties between 5:8- and 7:8-dihydro-α-naphthylamine, for only the latter is reduced to *ar*-tetrahydro-α-naphthylamine by treatment with sodium and ethyl alcohol in the absence of an indifferent solvent of high boiling point.

The present communication consists of a description of the means employed for the isolation of the pure dihydro-α-naphthylamines, the proof of their constitution, and the preparation of certain of their derivatives.

Owing to the close relationship between α-naphthylamine, its two dihydro-derivatives, and its tetrahydro-derivative, the discovery of a suitable derivative of these bases which, by possessing a distinctive crystalline form in each case, would afford a ready means of purification and characterisation, was highly desirable.

After a number of trials, it was found that the most suitable compound to prepare was the benzylidene derivative, which was readily obtained in a pure condition from each of the crude bases, and, moreover, by hydrolysis of the benzylidene derivatives, the bases were readily obtained in a pure state.

The following table shows the difference in melting point and crystalline form exhibited by the four benzylidene derivatives:

Benzylidene-α-naphthylamine.	Small, pearly plates.	m. p. 70—71°
Benzylidene-5 : 8-dihydro-α-naphthylamine.	Massive, rhombic pyramids with brachydomes and brachypinakoids.	m. p. 69°.
Benzylidene-7 : 8-dihydro-α-naphthylamine.	Long crystals which are a combination of a rhombic prism and pyramid with brachypinakoids.	m. p. 64°.
Benzylidenetetrahydro-α-naphthylamine.	Flat, rhombic prisms with brachypinakoids.	m. p. 61·5°.

The melting point of each of these compounds was depressed by admixture with any other.

It should be noted that, although *ar*-tetrahydro-α-naphthylamine has been frequently compared with *o*-2-xylidine in the past, as far as the formation of a crystalline benzylidene derivative is concerned, it is more strictly comparable with *p*-xylidine, as the isomeric xylidines form non-crystalline benzylidene derivatives. The benzylidene derivatives of the three hydrogenated bases readily form large crystals, and it is a simple matter to obtain well-formed crystals of these compounds weighing upwards of 1 gram each.

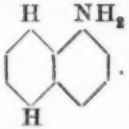
Both 5:8- and 7:8-dihydro-α-naphthylamine condense with diazonium salts, with the direct formation of aminoazo-compounds, and they may also be diazotised and combined with amines or phenols, forming azo-dyes, which differ in shade from similar azo-dyes derived from α-naphthylamine or *ar*-tetrahydro-α-naphthylamine. The relation of the shades of similar azo-dyes produced from the four amines by the two different methods is shown in the following table:

Naphthaleneazo-β-naphthol	Claret.
5:8-Dihydronaphthaleneazo-β-naphthol	Red, rather bluer than Para-Red.
7:8-Dihydronaphthaleneazo-β-naphthol	Orange-red.
Tetrahydronaphthaleneazo-β-naphthol.....	Orange.
p-Sulphobenzeneazo-α-naphthylamine	Reddish-brown.
p-Sulphobenzeneazo-5 : 8-dihydro-α-naphthylamine.	Brownish-yellow.
p-Sulphobenzeneazo-7 : 8-dihydro-α-naphthylamine.	Dull orange.
p-Sulphobenzeneazotetrahydro-α-naphthylamine	Vivid orange.

As the four acid dyes are very sensitive to acids, the shades are those produced after the dyed material had been soaped.

The shade produced by an azo-derivative of 5:8-dihydro-α-naphthylamine is more nearly related to that produced by a similar azo-derivative of α-naphthylamine, whilst the shade produced by a 7:8-dihydro-α-naphthylamine derivative is more nearly related to that produced by a similar tetrahydro-α-naphthylamine derivative.

Experimental.

5:8-*Dihydro-α-naphthylamine*,  .

The crude base was prepared from α-naphthylamine by the action of sodium and ethyl alcohol in the presence of an indifferent solvent of high boiling point (Farbenfabriken vorm. F. Bayer & Co., D.R.-P. 305347). A mixture of 400 c.c. of dry solvent naphtha (b. p. 139°) and 30 grams of sodium contained in a flask fitted with a reflux condenser was boiled, and a solution of 34 grams of α-naphthylamine in rather more dry ethyl alcohol than is necessary to dissolve the sodium added drop by drop through the condenser. Boiling was continued until all the sodium had disappeared; an excess of alcohol is desirable in order to complete the reaction as quickly as possible. The mixture was poured into water, the solvent naphtha layer separated, acidified with hydrochloric acid, and the solvent naphtha removed by distillation in a current of steam. The residue was filtered from a little tar and allowed to crystallise. The hydrochloride was basified, the base allowed to crystallise, and, after pressing well, it was melted with 10 per cent. of its weight of toluene, cooled in a freezing mixture of ice and salt, filtered quickly, and dried. It was converted into the benzylidene derivative by mixing 21 grams of the base with 15 grams of benzaldehyde, and allowing to remain until the mixture solidified. The product was pressed well and crystallised twice from light petroleum (b. p. 70°).

Benzylidene-5:8-dihydro-α-naphthylamine forms massive, rhombic pyramids with brachydomes and brachypinakoids, melting at 69° (corr.) (Found: C = 87·75; H = 6·51. $C_{17}H_{15}N$ requires C = 87·55; H = 6·44 per cent.).

The benzylidene derivative was hydrolysed by warming with hydrochloric acid, and the benzaldehyde removed by distillation in a current of steam. The residue, after filtration, was basified, and the base distilled.

5:8-*Dihydro-α-naphthylamine* forms large, colourless, rhombic plates or needles, melting at 37·5° (corr.) and boiling at 247°/408 mm., and the *hydrochloride* forms stout, colourless needles. Both the base and the hydrochloride turn pink on exposure to air (Found: C=82·59; H=7·65. $C_{10}H_{11}N$ requires C=82·76; H=7·58 per cent.).

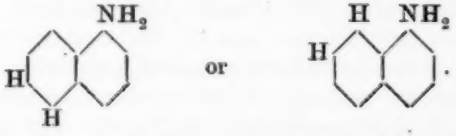
When the amine was diazotised and treated with an alkaline solution of sodium stannite, Δ^2- or 1:4-dihydronaphthalene, consisting of colourless plates melting at 24·5—25°, was obtained, which formed a compound with mercuric acetate, crystallising from benzene in colourless needles melting at 121°, and a dibromide, long, glistening, thin prisms melting at 71·5—72°.

5:8-*Dihydroaceto-α-naphthalide* crystallises from alcohol in colourless, silky needles melting at 163° (corr.). It may be sublimed unchanged (Found: C=77·15; H=7·01. $C_{12}H_{13}ON$ requires C=77·01; H=6·95 per cent.).

2:4-*Dinitrophenyl*-5:8-*dihydro-α-naphthylamine* was obtained by heating, under reflux, a mixture of 5 grams of the base, 6·9 grams of 4-chloro-*m*-dinitrobenzene dissolved in 100 c.c. of alcohol, and a solution of 4·6 grams of crystallised sodium acetate in a little water. The product crystallises from acetic acid or toluene in reddish-brown, rhombic plates melting at 144° (corr.) (Found: C=61·89; H=4·27. $C_{16}H_{13}O_4N_3$ requires C=61·74; H=4·18 per cent.).

The *sodium* salt of p-*sulphobenzeneazo*-5:8-*dihydro-α-naphthylamine* was obtained by the addition of diazotised sulphanilic acid to an aqueous solution of the hydrochloride of the base. The product, which separated as a crystalline precipitate, was dissolved in the minimum quantity of boiling dilute aqueous sodium carbonate, and, on cooling, the salt separated in glistening, brown plates.

5:6(or 7:8)-*Dihydro-α-naphthylamine*,



α-Naphthylamine was reduced to 5:8-dihydro-α-naphthylamine, as already described. When all the sodium had disappeared, the mixture was distilled until the internal temperature rose to 140°, and heating was continued at that temperature for one hour, during which period ammonia was evolved, owing to some decomposition of the amine. The mixture was poured into water, the

oily layer separated, acidified with hydrochloric acid, and the remainder of the solvent naphtha removed by distillation in a current of steam. The residue was filtered from tar and allowed to crystallise. The *hydrochloride* separated in straw-coloured, feathery needles, quite different in appearance from the less soluble hydrochloride of the isomeric base. The hydrochloride was basified, the base extracted with ether, and converted into the benzylidene derivative, as described for the isomeric compound.

Benzylidene-7:8-dihydro-α-naphthylamine separates from light petroleum in long crystals, which are a combination of a rhombic prism and pyramid with brachypinakoids, melting at 64° (corr.) (Found: C = 87·39; H = 6·48. $C_{17}H_{15}N$ requires C = 87·55; H = 6·44 per cent.).

The benzylidene derivative was hydrolysed by warming with hydrochloric acid, the benzaldehyde removed by extraction with ether, the solution of the hydrochloride basified, extracted with ether, and the base distilled.

7:8-Dihydro-α-naphthylamine is a colourless oil boiling at 180—182°/30 mm., which rapidly darkens on exposure to air, and is less stable than the isomeric base. It did not crystallise when maintained at −18° for a considerable time (Found: C = 82·66; H = 7·71. $C_{10}H_{11}N$ requires C = 82·76; H = 7·58 per cent.).

When the amine was diazotised and treated with a solution of alkaline sodium stannite, Δ^1- or 1:2-dihydronaphthalene, crystallising in colourless plates, melting at −9°, was obtained, which formed a compound with mercuric acetate of high melting point, insoluble in benzene, and a dibromide, stout, prismatic crystals melting at 70—71°.

7:8-Dihydroaceto-α-naphthalide forms colourless, silky needles melting at 153° (corr.). The yield was not good, owing to the instability of the amine at the temperature of acetylation (Found: C = 77·00; H = 7·01. $C_{12}H_{13}ON$ requires C = 77·01; H = 6·95 per cent.).

2:4-Dinitrophenyl-7:8-dihydro-α-naphthylamine was obtained in a similar manner to that used for the isomeric compound. It crystallises from acetic acid or toluene in glistening, reddish-brown leaflets or needles melting at 136° (corr.) (Found: C = 61·78; H = 4·13. $C_{16}H_{13}O_4N_3$ requires C = 61·74; H = 4·18 per cent.).

The *sodium* salt of *p-sulphobenzeneazo-7:8-dihydro-α-naphthylamine* was obtained in a similar manner to that used for the isomeric compound. It crystallises in reddish-brown, glistening plates.

ar-Tetrahydro-α-naphthylamine was readily obtained from 7:8-dihydro-α-naphthylamine by adding 15 grams of sodium to a

boiling solution of 10 grams of the base in 200 c.c. of dry ethyl alcohol. The mixture was worked up in the usual manner.

For purposes of comparison, *benzylidene*-ar-*tetrahydro*-α-*naphthylamine* was prepared from *ar*-tetrahydro-α-naphthylamine. It crystallises from light petroleum in flat, rhombic prisms with brachypinakoids, melting at 61·5° (corr.) (Found: C = 86·70; H = 7·33. $C_{17}H_{17}N$ requires C = 86·81; H = 7·23 per cent.).

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CLXXIV.—*The Formation and Stability of* spiro-*Compounds. Part III.* spiro-*Compounds from* cyclo*Pentane.*

By OSCAR BECKER and JOCELYN FIELD THORPE.

IN Part I of this series (Beesley, Ingold, and Thorpe, T., 1915, **107**, 1080) attention was directed to the fact that when the normal angle between two of the valencies of a carbon atom is changed as the result of their inclusion in a ring, groups attached by means of the other two valencies apparently take up an altered relative position. The hypothesis which was suggested in this connexion was that when two of the valencies, *a* and *b*, of a carbon atom are maintained by their participation in a ring at some inclination other than the normal, the two remaining valencies, *c* and *d*, will assume directions which enclose an angle differing from the normal in the opposite sense. In particular, if 2β be the angle formed by the valencies *a* and *b*, the angle 2θ between the directions taken up by the valencies *c* and *d* will be determined by the condition that these directions are equally inclined to each other and to the directions occupied by the valencies *a* and *b*. Thus, the angles between the lines of action of the following pairs of valencies, namely, *a* and *c*, *b* and *c*, *a* and *d*, *b* and *d*, are all equal to 2θ. From this condition, it follows that if 2β is greater than the normal angle (namely, the angle $2\tan^{-1}\sqrt{2} = 109°28'16''$ subtended at the centre of a regular tetrahedron by one of its sides), then 2θ will be less than this amount, and vice versa.

A general equation from which 2θ can be calculated when 2β is known may very readily be obtained by the following method.

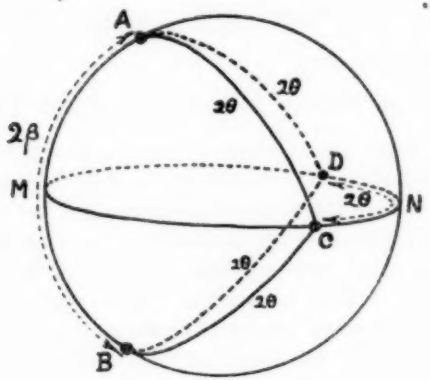
Let a small sphere (see figure) be described around the carbon atom as centre, and let the points A, B, C, and D, in which the lines of action of the valencies, a, b, c, and d cut the sphere, be joined by great circles. Let M and N be the two points of intersection of the great circle AB with the great circle CD, M being nearest A and B, and N nearest C and D. This construction involves the description of a number of right-angled spherical triangles, and a consideration of any of them, such as, for example, the triangle BCM, shows that

$$\cos 2\theta = \cos\beta \,.\, \cos(\pi - \theta).$$

The solution of this equation is

$$\cos\theta = \tfrac{1}{4}\{\sqrt{\cos^2\beta + 8} - \cos\beta\}$$

for all real values of the angles. The general character of this



solution is exhibited in the following table, in which 2θ is calculated for a number of values of 2β which the different alicyclic structures may be supposed to determine:

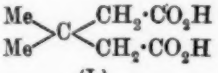
Ring.	2θ.			2β.		
*cyclo*Propane	60°	0′	0″	116°	55′	56″
*cyclo*Butane	90	0	0	112	58	44
*cyclo*Pentane	108	0	0	109	46	13
*cyclo*Hexane	120	0	0	107	14	58
*cyclo*Heptane.....	128	34	17	105	16	3
*cyclo*Octane	135	0	0	103	40	38
No ring	109	28	16	109	28	16

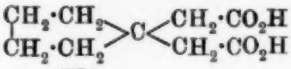
From this table it will be seen that in one case, namely, that corresponding with the *cyclo*pentane ring, the angle 2β differs from the normal angle by some minutes of arc only. This case, therefore, is of particular interest, since groups attached to two of the valencies of a carbon atom, the remaining two valencies of

which are bound in a *cyclo*pentane ring, should differ but little in their reactions, and particularly in their interactions, from corresponding groups in a similar structure from which the *cyclo*pentane ring is absent.

The present communication deals with this case, the comparison instituted being between ββ-dimethylglutaric acid (I) on the one hand and *cyclo*pentane-1 : 1-diacetic acid (II) on the other, and it is shown that the reactions of derivatives of the latter acid follow very closely the analogies presented by the corresponding derivatives of the former.

In Part I, the result of an experimental study of *cyclo*hexane-1 : 1-diacetic acid (III) was described, and it was shown that the


(I.)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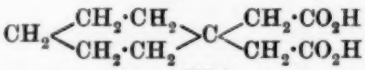
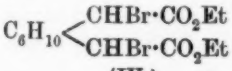

(III.)

behaviour of certain derivatives of this substance differed very notably from that of the corresponding members of the dimethylglutaric series. The principle points of contrast presented themselves in connexion with:

(*a*) The unstable character which the dibromo-ester of *cyclo*hexane-1 : 1-diacetic acid (IV) possesses, owing to the tendency it has to eliminate ethyl bromide and to pass into the bromo-lactone ester (V), whereas the corresponding dibromo-ester of ββ-dimethylglutaric acid (VI) is stable.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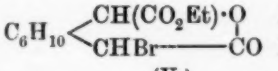
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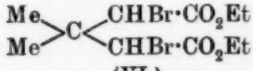
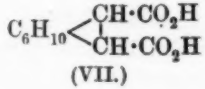

(VI.)

(*b*) The great stability of *cyclo*hexane*spirocyclo*propanedicarboxylic acid (VII), which, for example, resists the action of concentrated hydrochloric acid at 240°, whereas the corresponding dimethyl*cyclo*propanedicarboxylic acid (caronic acid) (VIII) is transformed into terebic acid (IX) by 5 per cent. acid at 200°.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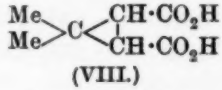
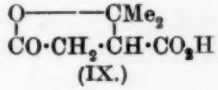
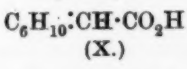

(VIII.)


(IX.)


(X.)

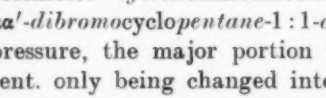
(*c*) The tendency to the formation of *cyclo*hexylideneacetic acid (X) when the bromo-lactone ester is treated with alkalis.

Clearly the fact that groups can be eliminated from the acetic acid residues more readily in the *cyclo*hexanediacetic series than in the dimethylglutaric series, and also the fact that the products formed by the establishment of a bond between the residues are more stable in the *cyclo*hexane series, are both in full accord with the idea that the acetic acid residues are closer together in the *cyclo*hexanediacetic series than in the dimethylglutaric series, as the calculation of 2β for the *cyclo*hexane ring indicates. On the other hand, the relation which the conversion of the bromo-lactone ester into *cyclo*hexylideneacetic acid, large quantities of which are produced under widely varying conditions,* bears to molecular structure, is not very clear, although it is doubtless connected with the greater stability which, according to the hypothesis here put forward, the *cyclo*hexane ring should bestow on the semi-cyclic double bond when comparison is made with the double bond in dimethylacrylic acid, $CMe_2{:}CH{\cdot}CO_2H$.

On the basis of the hypothesis outlined, one would therefore expect that, in regard to the elimination of the groups from the acetic acid residues, and also in regard to the stability of the products in which a bond has been established between the acetic acid residues, and as regards the tendency to the formation of an unsaturated monobasic acid, the derivatives of *cyclo*pentanediacetic acid would resemble those of dimethylglutaric acid rather than those of *cyclo*hexanediacetic acid, in spite of the fact that in molecular weight and in cyclic structure *cyclo*pentanediacetic acid comes closer to the latter. Actually, the expectation has been realised.

In particular, it is shown in the present paper that:

(*a*) As regards the stability of its dibromo-ester, *cyclo*pentanediacetic acid resembles dimethylglutaric acid more closely than it resembles *cyclo*hexanediacetic acid. Thus, on distilling *ethyl* $\alpha\alpha'$*-dibromo*cyclo*pentane*-1 : 1-*diacetate* (XI) under diminished pressure, the major portion passes over unchanged, some 10 per cent. only being changed into the *bromo*-ester (XII). In similar circumstances, the *cyclo*hexane bromo-ester is completely converted into the bromo-lactone ester and ethyl bromide. Ethyl dibromodimethylglutarate, in small quantities, distils practically without



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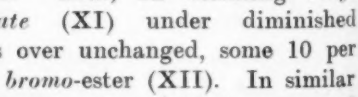
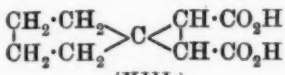


(XII.)

* Under certain conditions, however, the *cyclo*hexylideneacetic acid itself becomes unstable and passes quantitatively into the isomeride with the double bond in the ring. This is therefore the product actually isolated in the circumstances (*loc. cit.*).

decomposition, although the corresponding bromo-lactone ester can be obtained by repeated slow distillation.

(*b*) *cyclo*Pentane*spirocyclo*propane-1 : 2-dicarboxylic acid (XIII) does not possesses the same general stability as the corresponding *cyclo*hexane derivative. Thus, whilst the latter is stable to concentrated hydrochloric acid at 240°, the former is rapidly decomposed, even at 200°, by 5 per cent. acid. Under these conditions, the dimethyl analogue, caronic acid, is also decomposed.



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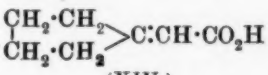

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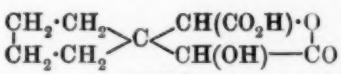


(XV.)

(*c*) *cyclo*Pentylideneacetic acid (XIV) can be isolated from the product obtained by hydrolysing the bromo-lactone ester (XII) with alkalis. It is, however, apparently formed in very much smaller amount than is the case with the corresponding *cyclo*hexylidene derivative. In the dimethylglutaric series, this curious reaction has not yet been observed at all, and, indeed, it may be peculiar to cyclic compounds.

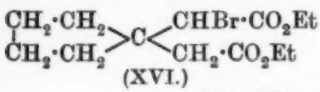
In view of these results, the chemistry of *cyclo*pentanediacetic acid and its derivatives may be said to come well into line with the general view which forms the present working hypothesis underlying the experiments recorded in this series of papers.

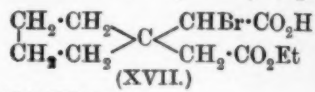
Ethyl **αα′**-dibromo*cyclo*pentane-1 : 1-diacetate (XI) is produced by the action of phosphorus pentabromide and bromine on the anhydride of *cyclo*pentane-1 : 1-diacetic acid (XIX), and subsequent treatment with alcohol. From this, a considerable quantity of the bromo-lactone ester (XII) can be obtained by repeated distillation. The lactone, on hydrolysis with 25 per cent. aqueous potassium hydroxide, yields two compounds, namely, *cyclo*pentylideneacetic acid (XIV) (Wallach, *Annalen*, 1902, **323**, 159; 1906, **347**, 324; Harding and Haworth, T., 1910, **97**, 493) and the *lactonic acid* of **αα′**-*dihydroxy*cyclo*pentane*-1 : 1-*diacetic acid* (XV).

The similarity between the open-chain series and that containing the five-membered ring is also shown in the behaviour of the diacetic acids towards mono-bromination. Thus the mono-bromination of *cyclo*pentanediacetic acid leads to the formation of *ethyl* **α**-*bromo*cyclo*pentane*-1 : 1-*diacetic acid* (XVI), in the same manner as dimethylglutaric acid yields ethyl α-bromodimethylglutarate. It will be noted that the α-brominated ester of *cyclo*-

hexane-1:1-diacetic acid could not be obtained (T., 1915, **107**, 1084).

In the cases of both dibromination and monobromination, besides the neutral esters obtained, one and the same *acid* (XVII) is pro-


(XVI.)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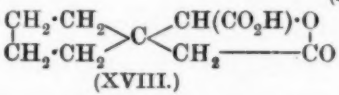
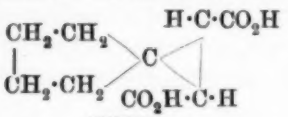

(XVIII.)

duced. The acid product of bromination, as well as the neutral ester, on treatment with highly concentrated potassium hydroxide solution, yields, in addition to the *lactone* of *α-hydroxy*cyclo*pentanediacetic acid* (XVIII), both the *trans-* and *cis*-modifications of the *spiro*-acid (XIII) and (XX).

trans-cyclo*Pentane*spirocyclo*propane*-1:2-*dicarboxylic acid*, on distillation under atmospheric pressure, yields the *anhydride* (XIX) of its *cis*-isomeride, from which the *cis*-acid (XX) can be obtained in the usual manner.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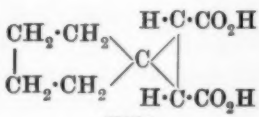
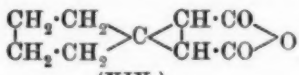

(XX.)


(XIX.)

It should be added for the benefit of those who may wish to prepare the substances described in this paper that many difficulties were encountered, owing to the remarkable lack of tendency to crystallise which they exhibit. At one time it was thought that the research would have to be abandoned for this reason, but, owing to its importance in relation to the general scheme of work at present being undertaken in these laboratories, it was necessary that every effort should be made to bring it to a successful conclusion. As will be seen from the experimental portion, this was ultimately accomplished, although in some cases the compounds described became crystalline only after keeping for several months.

Experimental.

Dibromination of cyclo*Pentane*-1:1-*diacetic Acid.*

Dibromination was effected by treating 23·2 grams of the acid, prepared by Kon and Thorpe's method (T., 1919, **115**, 700), with

115 grams of phosphorus pentabromide, and, after a clear solution had been obtained by gentle heating on the water-bath, adding gradually 43 grams of bromine. The interaction was completed by heating until the halogen had disappeared, and, when cold, the dibromo-acid bromide was poured into 500 c.c. of well-cooled absolute alcohol. The oil, which was precipitated by water, was extracted by ether, and the ethereal extract thoroughly shaken with dilute aqueous sodium carbonate solution to remove acid products. The ether was then evaporated. *Ethyl* **aa'**-*dibromo*cyclo*pentane*-1 : 1-*diacetate* (XI) boils at 211—212°/30 mm., and is a colourless, fairly mobile oil (Found: Br = 39·39. $C_{13}H_{20}O_4Br_2$ requires Br = 40·0 per cent.).

aa'-*Dibromo*cyclo*pentane*-1 : 1-*diacetic acid*,

$$C_4H_8{:}C(CHBr{\cdot}CO_2H)_2,$$

is obtained as a white, crystalline precipitate when the dibromo-acid bromide obtained in the above experiment is poured into formic acid. It separates from formic acid in small prisms, which melt at 177° (Found: Br = 46·43. $C_9H_{12}O_4Br_2$ requires Br = 46·5 per cent.).

Lactone of Ethyl **α**-*Bromo*-**α**-*hydroxy*cyclo*pentane*-1 : 1-*diacetate* (XII).

The mixed *cis*- and *trans*-lactones of this formula are produced by the repeated distillation of the dibromo-ester, whereby ethyl bromide is also formed. The mixture boils at 220—222°/25 mm., and is a colourless, viscid oil (Found: Br = 27·71. $C_{11}H_{15}O_4Br$ requires Br = 27·5 per cent.).

As the lactones showed no tendency to crystallise, we were unable to separate the *cis*- and *trans*-isomerides.

Hydrolysis of the Bromo-lactone. (a) cyclo*Pentylideneacetic Acid* (XIV).—This acid can be prepared in small yield by hydrolysing 12 grams of the lactone by means of 60 c.c. of a 25 per cent. aqueous potassium hydroxide at the boiling point for two hours. The clear solution is evaporated to a small bulk and acidified, when the unsaturated acid separates, and can be purified by recrystallisation from water. It melts at 52° (Found: C = 66·53; H = 7·94. Calc.: C = 66·7; H = 7·9 per cent.).

(b) *The lactonic acid of* **aa**-*dihydroxy*cyclo*pentane*-1 : 1-*diacetic acid* (XV) is obtained from the filtrate after the separation of *cyclo*pentylideneacetic acid by extracting it, after saturation with ammonium sulphate, with ether. The product left when the ether is evaporated is a gum, which solidified only after being kept for some months. It crystallises from benzene in small, colourless

prisms, which melt at 139—140° (Found: C = 53·88; H = 5·98. $C_9H_{12}O_5$ requires C = 54·0; H = 6·0 per cent.).

The melting point of this compound would suggest that it is the *trans*-modification, corresponding with the *trans*-modification of the higher homologue (T., 1915, **107**, 1100), which melts at 145°.

Monobromination of cyclo*Pentane*-1 : 1-*diacetic Acid.*

Twenty-six grams of *cyclo*pentanediacetic anhydride, prepared by treating the acid with acetyl chloride (T., 1919, **115**, 700), were mixed with 80 grams of phosphorus pentabromide and 28 grams of bromine added, the process of bromination being the same as that already described in the case of dibromination.

(1) *The Neutral Product of Bromination. Ethyl* **αα'**-*Bromo*cyclo*pentane*-1 : 1-*diacetate* (XVI).—The ester was distilled under diminished pressure and obtained as a nearly colourless oil, which, however, was shown by analysis to contain a small quantity of unbrominated ethyl ester, or possibly the corresponding lactone ethyl ester. Ultimately, it was found that a comparatively pure product could be obtained by using 9 per cent. excess of bromine (that is, 31 grams instead of 28). The ester produced in this way boiled at 192°/17 mm. (Found: Br = 25·43. $C_{13}H_{21}O_4Br$ requires Br = 24·9 per cent.).

(2) *The Acid Product of Bromination. Ethyl Hydrogen* **α**-*Bromo*cyclo*pentane*-1 : 1-*diacetic Acid* (XVII).—This acid ester is identical with the one produced by acidifying the sodium carbonate extract from the dibromination experiment. In the present instance, it is obtained in the same manner from the monobrominated product. It cannot be distilled without decomposition, but gave a fairly good analysis in the crude state (Found: Br = 26·12. $C_{11}H_{17}O_4Br$ requires Br = 27·2 per cent.).

The Action of Alkalis. (a) *The Lactone of* **α**-*Hydroxy*cyclo*pentane*-1 : 1-*diacetic Acid* (XVIII).—By the action of boiling aqueous sodium carbonate on the above acid product of bromination, the lactone is obtained as sole product. Eight grams of the crude acid bromo-ester were hydrolysed by boiling for six hours with a solution containing 4·5 grams of anhydrous sodium carbonate in 45 c.c. of water. The clear solution obtained in this way was extracted repeatedly with ether, the ethereal solution yielding 5 grams of a viscid gum on evaporation. This material distilled at 228—230°/15 mm., but several months elapsed before it commenced to crystallise. It is freely soluble in all the usual organic solvents with the exception of light petroleum, in which it is insoluble, and can be purified by treatment with the 40—60°

fraction of this solvent, when it is obtained as a white, crystalline powder melting at 69—70° (Found: C = 58·59; H = 6·65. $C_9H_{12}O_4$ requires C = 58·7; H = 6·6 per cent.).

The *silver* salt of the corresponding dibasic acid is precipitated when silver nitrate solution is added to a solution of the ammonium salt which has been prepared by heating a solution of the lactone in excess of dilute ammonia (Found: Ag = 51·90. $C_9H_{12}O_5Ag_2$ requires Ag = 51·9 per cent.).

trans-cyclo*Pentane*spirocyclo*propane*-1 : 2-*dicarboxylic Acid* (XIII).

This *spiro*-acid is best prepared by the action of very concentrated aqueous potassium hydroxide on the acid bromo-ester, but it can also be prepared from the neutral bromo-ester if the right conditions are observed.

(a) *From the Acid Bromo-ester.*—A solution containing 60 grams of potassium hydroxide in 50 c.c. of water was heated until the temperature reached 150°, when 19 grams of the acid product of bromination were cautiously added as rapidly as possible, and the vigorous reaction was allowed to subside. When cold, the solid mass was dissolved in water and acidified with hydrochloric acid, when crystals of the *spiro*-acid separated on cooling.

(b) *From the Neutral Bromo-ester.*—Fifteen grams of the neutral monobromo-ester were mixed with an alcoholic potassium hydroxide solution containing 15 grams of the hydroxide in 9 c.c. of water and 60 c.c. of absolute alcohol, and heated for ten hours. The solution, freed from alcohol, yielded the *spiro*-acid on acidification. The acid crystallises from water in colourless plates melting at 211° (Found: C = 58·79; H = 6·46. $C_9H_{12}O_4$ requires C = 58·7; H = 6·6 per cent.).

The *silver* salt is a white, crystalline powder (Found: Ag = 54·19. $C_9H_{10}O_4Ag_2$ requires Ag = 54·2 per cent.).

The *dianilide*, $C_4H_8{:}C\begin{<}\mathrm{CH{\cdot}CO{\cdot}NHPh}\\ \mathrm{CH{\cdot}CO{\cdot}NHPh}\end{>}$, was prepared by heating the acid with excess of aniline at 200° for two hours, and recrystallising the product from dilute alcohol. It forms white, silky needles melting at 289° (Found: C = 75·34; H = 6·71. $C_{21}H_{22}O_2N_2$ requires C = 75·4; H = 6·6 per cent.).

cis-cyclo*Pentane*spirocyclo*propane*-1 : 2-*dicarboxylic Acid* (XX).

The filtrate from the *trans*-acid was extracted repeatedly with ether, the ethereal solution yielding a gum on evaporation, which became partly solid on keeping. This was found to be a mixture

of the lactone (XVIII) and the *cis*-acid, from which the latter could be separated by spreading on a porous plate. The *cis*-acid is, however, best prepared by distilling the *trans*-acid under diminished pressure and treating the anhydride of the *cis*-acid which is then formed with water. The *cis-spiro*-acid crystallises from a small quantity of water in white, flattened prisms, which melt at 170°. It is much more readily soluble in water than the *trans*-isomeride (Found: C = 59·03; H = 6·55. $C_9H_{12}O_4$ requires C = 58·7; H = 6·6 per cent.).

The *anhydride of the* cis-*acid* (XIX) was prepared by the action of acetyl chloride on the *cis*-acid, and also, as mentioned above, by distilling the *trans*-acid under diminished pressure. As it showed no tendency to crystallise, it was characterised by conversion into the *anilic acid*, $C_4H_8{:}C\begin{<}\begin{matrix}CH\cdot CO\cdot NHPh\\ CH\cdot CO_2H\end{matrix}$, by treating it in benzene solution with the calculated quantity of aniline. It crystallises from dilute alcohol in small needles, which melt at 187° (Found: C = 69·40; H = 6·62. $C_{15}H_{17}O_3N$ requires C = 69·5; H = 6·6 per cent.).

The Stability of the trans-*Modification*.—It was soon seen that the *trans*-acid was very much less stable towards concentrated hydrochloric acid at 250° than the corresponding *cyclo*hexane derivative, for, under these conditions, it was found to undergo complete decomposition. The action of 5 per cent. acid was therefore tried, and it was found that, whereas at 150° the acid remained unchanged, even on prolonged heating, at 200° it was completely decomposed in the course of an hour. Under the conditions, therefore, which transform caronic acid into terebic acid, the *trans-cyclo*pentane*spiro*-acid is broken down into several products, of which free carbon is the chief. The *cis*-acid behaved in the same way, although there was evidence that it was partly transformed into the *trans*-acid prior to decomposition. Otherwise, the *trans*-acid, like similar acids of the series, is remarkably stable. It can, for example, be boiled for a short time with acid permanganate without change, and is stable to alkaline permanganate in the cold.

In conclusion, we wish to express our thanks to Mr. C. K. Ingold and to Mr. G. A. R. Kon for much help in this very difficult piece of experimental work during the absence of one of us abroad.

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SOUTH KENSINGTON. [*Received, October 26th*, 1920.]

CLXXV.—*Disodium Hydrogen Phosphate Dodecahydrate.*

By Dalziel Llewellyn Hammick, Hector Kenneth Goadby, and Henry Booth.

The system disodium hydrogen phosphate–water has been investigated by Shiomi (*Mem. Coll. Sci. Eng. Kyoto*, 1908, i, 406), who showed that three hydrates ($Na_2HPO_4,12H_2O$, $Na_2HPO_4,7H_2O$, $Na_2HPO_4,2H_2O$) are capable of existence in contact with saturated aqueous solutions at different temperatures. In the neighbourhood of 100°, anhydrous salt is the stable solid phase.

Shiomi records the following invariant points (breaks in a solubility curve):

Solid Phases.	Temperature.
$Na_2HPO_4,12H_2O$–$Na_2HPO_4,7H_2O$.	36·45°
$Na_2HPO_4,7H_2O$–$Na_2HPO_4,2H_2O$.	48·0
$Na_2HPO_4,2H_2O$–Na_2HPO_4	95·2

The eutectic temperature (ice, $Na_2HPO_4,12H_2O$–solution) is given as −0·45° by Rüdorf, *Ann. Phys. Chem.*, 1864, [ii], **122**, 337) and as −0·9° by Guthrie ("Recueil de Const. Phys.").

Certain peculiarities of the dodecahydrate having led to the suspicion that Shiomi's analysis of the system was incomplete, the various hydrates were examined by means of heating and cooling curves. Arsenic-free dodecahydrate was recrystallised, and preparations of the other hydrates were made from it. The dihydrate is conveniently prepared by boiling the finely powdered dodecahydrate with ethyl alcohol. The heptahydrate was prepared by fusing together the appropriate mixture of dodecahydrate and dihydrate, and cooling.

The finely powdered hydrates were suspended in xylene and stirred with a thermometer in jacketed tubes immersed in a glycerol bath.

Well-defined arrests were obtained on the heating and cooling curves at the following temperatures:

$Na_2HPO_4,2H_2O$–Na_2HPO_4: 95·20, 94·92, 95·00, 94·90, 94·92 (corrected); mean, 94·97°.

$Na_2HPO_4,7H_2O$–$Na_2HPO_4,2H_2O$: 48·5, 48·0, 48·0, 47·8, 48·0, 48·2; mean, 48·09°.

$Na_2HPO_4,12H_2O$–$Na_2HPO_4,7H_2O$: 35·0, 35·1, 35·4, 35·0, 35·0, 35·05, 35·0, 35·0, 35·6, 35·05; mean, 35·0°.

At the same time, sharp breaks in the heating and cooling curves for the dodecahydrate were observed at 29·6° (29·6, 29·6,

29·5, 29·55, 29·65°). From these results, it appeared that Shiomi's points at 95·2° and 36·45° were probably too high. The transition temperature at 35·0° found by the authors is in agreement with Tilden's (T., 1884, **45**, 409). It seemed, moreover, likely that the break in the heating and cooling curves observed at 29·6° indicated a change of phase at that temperature.

In order to test this conclusion, crystals separating from a solution of sodium phosphate at 33° were collected and examined. They closely resemble in appearance the ordinary large, monoclinic crystals obtained at the ordinary temperatures; on keeping, however, in a closed tube at the ordinary temperatures (15—20°), they become opaque and friable. Analysis of the clear crystals gave the following result: 2·3910 grams gave 0·7505 gram of magnesium pyrophosphate, whence the number of molecules of water of crystallisation for one molecule of disodium hydrogen phosphate is 11·95.

The solid phase in equilibrium with solutions between 29·6° and 35·0° is therefore a dodecahydrate. Crystals of ordinary dodecahydrate kept in a closed tube in a thermostat above 29·6° (at 33°) slowly lose their transparency and rigidity, whereas crystals formed between 29·6° and 35·0° undergo no change.

The conclusion is therefore drawn that disodium hydrogen phosphate dodecahydrate exists in two forms, α and β, the α-form being stable between 29·6° and 35·0°, and the ordinary, or β-form, below 29·6°.

Shiomi's solubility data (*loc. cit.*) give no indication of any change in the solid phase in equilibrium between 0° and 36·5°. Solubilities were therefore redetermined from the eutectic temperature to above the transition temperature of the α-dodecahydrate into heptahydrate.

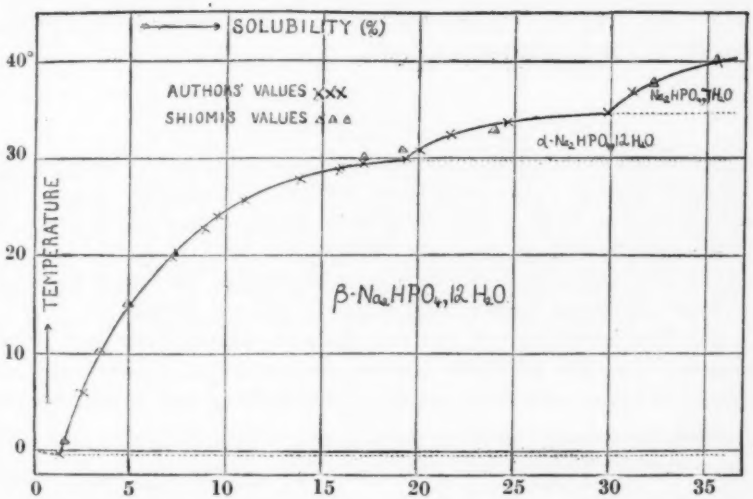
The temperature of the eutectic was found by stirring solutions of sodium phosphate in freshly distilled water in jacketed tubes cooled in a brine-bath at $-3·0°$ to $-4·0°$. Steady temperatures* were obtained at the following points, which remained unchanged for at least half a minute on removing the tube from the brine-bath: $-0·42°$, $-0·47°$, $-0·47°$, $-0·47°$. In the first two experiments, the solid phase separating first was ice. In order to determine the composition of the liquid phase at the eutectic, a solution that had been brought to the eutectic point was stirred in a freezing mixture of ice and sodium phosphate for about half an hour, solid matter allowed to settle, and about 5 grams of the supernatant liquid were removed with a pipette and analysed.

* The thermometer was graduated in 1/50° and was standardised before use.

The result is shown in the table below. The other solubilities there given were determined as follows.

Saturated solutions were prepared by stirring the appropriate solid phase with distilled water in an electrically heated and controlled thermostat, temperature being constant to within ±0·02°.

In order to make certain that the true solid phase in equilibrium was present during the whole period of stirring, an approximately saturated solution was prepared at a higher temperature than that of the thermostat and introduced into the solubility apparatus, together with a few crystals of the expected solid phase. Stirring was continued for three to four hours,* a portion of the saturated solution being then siphoned through a glass-wool filter into a



small weighed bottle. The whole operation was carried out in the thermostat.

The composition of the saturated solution was determined by conversion of the dissolved phosphate into magnesium pyrophosphate. The temperature of the thermostat was recorded with standard thermometers graduated in 1/20°, the mercury thread being totally immersed. Seventeen determinations were completed; two results were discarded, owing to suspicion of leakage of water from the thermostat into the solubility apparatus. The remainder are given below as grams of anhydrous disodium hydrogen phosphate in 100 grams of solution.

* It was found that no difference greater than 0·05 per cent. was produced in the value of a solubility by continuing the stirring for eight hours.

Temperature.	Solubility.	Temperature.	Solubility.
−0·47° (eutectic).	1·45	+29·50°	17·18
+6·00 *	2·73	30·10	19·45
19·95	7·26	30·90	20·08
22·77	8·93	32·50	22·57
24·15	9·53	33·70	24·63
25·75	10·90	34·70	29·75
27·80	14·16	36·50	31·15
28·65	15·87	40·02	35·56
29·05	16·04		

* Temperature at which a solution containing 2·81 grams in 100 grams of water begins to crystallise.

These results are plotted in the figure. The solubility curve shows distinct breaks at 29·5—29·6°, corresponding with the invariant point α-$Na_2HPO_4,12H_2O$–β-$Na_2HPO_4,12H_2O$–solution, and at 35·0°, corresponding with α-$Na_2HPO_4,12H_2O$–$Na_2HPO_4,7H_2O$–solution.

Summary.

(1) Disodium hydrogen phosphate dodecahydrate exists in two forms, α and β. The transition temperature between the α- and β-hydrates is 29·6°. The α-hydrate passes into heptahydrate at 35·0° (not 36·45°, as given by Shiomi, *loc. cit.*).

(2) The eutectic point, β-dodecahydrate–ice, is found to be at −0·47°, agreeing closely with Rüdorf's value, −0·45° (*loc. cit.*).

(3) The solubilities of the two dodecahydrates have been determined; from the solubility curves, the transition temperatures are found to agree with those deduced from heating and cooling curves.

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[*Received, November 15th*, 1920.]

CLXXVI.—*The Preparation of Ethyl Iodide.*

By BEATRICE ELIZABETHA HUNT.

THE preparation of ethyl iodide has recently been investigated by Adams and Voorhees (*J. Amer. Chem. Soc.*, 1919, **41**, 789), who recommend the employment of Walker's method (T., 1892, **61**, 717) in a slightly modified form. An alternative method, however, appeared possible in view of the work of Beilstein and Rieth (*Annalen*, 1863, **126**, 250), and this process forms the subject of the present communication.

Experiment showed that with the use of 80 per cent. alcohol in place of absolute alcohol, the vigour of the reaction, caused by the addition of iodine, was so much reduced that the time required to mix 500 grams of iodine with the requisite amount of alcohol and red phosphorus was not more than twenty minutes. Further, the yield was not affected by the omission of the customary period of keeping at the ordinary temperature, but boiling under reflux for two and a-half hours, followed by immediate distillation, was sufficient to ensure a good yield. The use of a large excess of alcohol is often suggested, but this proved unnecessary, and, indeed, rendered the process of purification more difficult, and thus reduced the yield.

In most modern text-books, the main reaction is regarded as taking place according to the equation

$$P + 3I + C_2H_6O = 3C_2H_5I + P(OH)_3,$$

but Beilstein (*loc. cit.*) interprets it thus:

$$P + 5I + C_2H_6O = 5C_2H_5I + H_3PO_4 + H_2O.$$

Estimations of the amount of unused phosphorus remaining after distillation agreed with this interpretation, which was further verified by the preparation of ethyl iodide, using the amount of phosphorus required by Beilstein's equation, when a good yield was obtained. In practice, however, it proved better to use an excess of phosphorus to ensure purity of the product.

Experimental.

To 500 grams of iodine in a flask of 4 litres capacity, cooled by water, about 281 grams of 80 per cent. alcohol (by weight) were added, and thereafter, during the course of about twenty minutes, 50 grams of red phosphorus, with shaking after each addition to ensure complete mixing. The first additions of phosphorus caused evolution of heat and boiling of the liquid in the flask, but no loss of vapour occurred. A reflux condenser was then attached to the flask, and the latter heated in a water-bath, so that the contents boiled gently. After about two and a-half hours, iodine vapour was no longer visible, although the mixture remained dark in colour. The ethyl iodide was, without cooling, distilled off, through a short, two-bulb condensing column, by heating, first in a water-bath and afterwards on a brine-bath. All the distillate passed over at 63—83°, and was colourless, except for a small fraction at the end, which had a yellow tinge. A few drops of sodium carbonate solution were added to ensure absence of free hydriodic acid, and a few drops of a dilute solution of sodium thiosulphate

to remove any free iodine, since ethyl iodide purified with sodium thiosulphate was proved to darken less quickly on keeping than when sodium carbonate alone was used, and the purification was accomplished more rapidly. The oil was then washed with water, dried over calcium chloride, and redistilled. The yield was 566 grams (92 per cent. of the theoretical), and the unused red phosphorus amounted to 24·45 grams.

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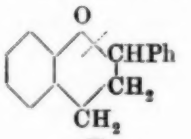
[*Received, October 25th*, 1920.]

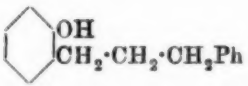
CLXXVII.—*Studies in the Chroman Series. Part I.*

By ANNIE GREENWOOD and MAXIMILIAN NIERENSTEIN.

IN order to obtain confirmatory evidence of the views expressed by one of us with regard to the action of metallic sodium and alcohol on catechin tetramethyl ether (this vol., pp. 971, 1151), we thought it advisable to study the effect of these reagents on some simple derivatives of the chroman series. Our observations on 1-phenylchroman (I) and 3-phenylchroman (III), which are described in the present communication, confirm in every respect the deductions made in the case of catechin tetramethyl ether. Thus we obtained 2-hydroxy-αγ-diphenylpropane (II) and 2-*hydroxy-αα-diphenylpropane* (IV) by the action of metallic sodium on 1-phenylchroman (I) and 3-phenylchroman (III) respectively. We also found that, whereas the αγ-derivative (II) is recovered unchanged on oxidation, 2-hydroxy-αα-diphenylpropane (IV) yields under the same conditions 2-hydroxydiphenylacetic acid (V).



(I).



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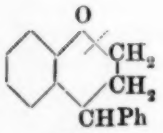
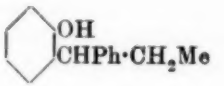
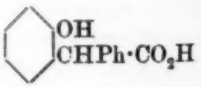


(III.)



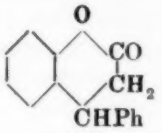
(IV.)



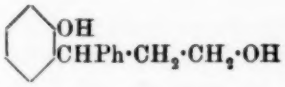
(V.)

1-Phenylchroman (I) has been previously prepared by Harries and Busse (*Ber.*, 1896, **29**, 380), and Feuerstein and Musculus

(*ibid.*, 1901, **34**, 412). We have obtained 3-*phenylchroman* (III) according to Semmler's scheme for the synthesis of chroman (*Ber.*, 1906, **39**, 2855). 3-Phenyldihydrocoumarin (VI) was reduced to 2-*ω-dihydroxy-αα-diphenylpropane* (VII), and subsequently converted into 3-phenylchroman (III).



(VI.)



(VII.)

Experimental.

2-*Hydroxy-αγ-diphenylpropane* (II).

To a solution of 11·5 grams of 1-phenylchroman, prepared according to Harries and Busse's method, in 150 c.c. of alcohol are added 50 grams of metallic sodium, and the solution is heated for eight hours on a water-bath. The alcohol is removed with steam, and, at the same time, 4·5 grams of unchanged 1-phenylchroman are recovered. This unchanged material is again reduced, 20 grams of sodium and 100 c.c. of alcohol being used. The combined aqueous solutions are extracted with ether in order to remove any unchanged 1-phenylchroman (0·72 gram of unchanged product was recovered on evaporation of the ether), the solution acidified with dilute sulphuric acid, and extracted several times with ether. The dried ethereal extract leaves, on evaporation, an oil, which solidifies on keeping over paraffin in a vacuum. It crystallises from light petroleum in slender, glistening needles, which melt sharply at 21·5°. The alcoholic solution turns violet with alcoholic ferric chloride. The yield is 69 per cent. of the theoretical (Found*: C=85·1; H=7·6. $C_{15}H_{16}O$ † requires C=84·9; H=7·5 per cent.).

Diazomethane converts the ethereal solution into the *methyl ether*, the yield being 86 per cent. of the theoretical. It is a viscous, colourless oil, which boils at 143—147°/11—12 mm. (Found ‡: C=84·9; H=8·2. $C_{16}H_{18}O$ requires C=85·0; H=7·9 per cent.).

* Dried over paraffin in a vacuum.

† Braun and Deutsch (*Ber.*, 1912, **45**, 2187) have prepared 2-hydroxy αγ-diphenylpropane in a different manner. They describe it as a yellow, viscous, odourless oil, which boils at 198—202°/15 mm. They calculate, however, wrongly for $C_{15}H_{12}O$, which requires C = 86·5; H = 5·8, and they find C = 85·63; H = 6·01 per cent.

‡ Dried over paraffin in a vacuum.

3-Phenyldihydrocoumarin (VI).

This substance has been prepared by Liebermann and Hartmann (*Ber.*, 1891, **24**, 2582) and Simonis ("Die Cumarine," 1916, p. 132), but neither method was used by us. We have prepared it by the action of acetyl chloride on 2-methoxy-$\beta\beta$-diphenylpropionic acid (compare Stoermer and Friderici, *Ber.*, 1908, **41**, 340). For the synthesis of this acid we used Fosse's method (*Ann. Chim.*, 1920, [ix], **13**, 105), which seemed to us preferable to that employed by Stoermer and Friderici (*loc. cit.*, p. 335).

Twenty-six grams of 2-methoxydiphenylcarbinol (prepared according to Stoermer and Friderici's method, *loc. cit.*, p. 332) are heated in an oil-bath for four hours at 120° with 50 grams of ethyl malonate. The excess of the ethyl malonate is distilled off and the solid crystallised from alcohol, from which it separates in long, prismatic needles, which melt at 134—135°, carbon dioxide being evolved (compare Stoermer and Friderici, *loc. cit.*, who give 131°). The yield is 92 per cent. of the theoretical.

2-Methoxy-$\beta\beta$-diphenylpropionic acid (23 grams) dissolved in glacial acetic acid (100 c.c.) is converted into 3-phenyldihydrocoumarin with acetyl chloride (15 grams) on keeping for forty-eight hours at the ordinary temperature. The precipitate formed on the addition of water contains some unchanged 2-methoxy-$\beta\beta$-diphenylpropionic acid, which is removed by dissolving the precipitate in ether and washing the ethereal solution with a 10 per cent. solution of sodium hydrogen carbonate saturated with carbon dioxide. The solid left on evaporation of the dried solution crystallises from alcohol in stout plates, which melt at 82°, as given by Liebermann and Hartmann (*loc. cit.*).

2-ω-Dihydroxy-αα-diphenylpropane (VII).

To a solution of 22 grams of 3-phenyldihydrocoumarin in 175 c.c. of alcohol, 50 grams of metallic sodium are added, and the solution is kept at the boiling point for eight hours, when all the sodium disappears. The solution, freed from alcohol by steam distillation, is acidified, extracted with ether, and the dried ethereal extract leaves, on evaporation, an oil, yielding a main fraction, which boils at 195—204°/11—12 mm. On redistillation of this fraction, a colourless, heavy oil is obtained, which boils constantly at 197—199°/11 mm. It is soluble in the usual organic solvents, and does not solidify even on prolonged keeping in a freezing mixture. The yield is 68 per cent. of the theoretical (Found *: C = 79·1; H = 7·3. $C_{15}H_{16}O_2$ requires C = 78·9; H = 7·0 per cent.).

* Dried over paraffin in a vacuum.

3-Phenylchroman (III).

A solution of 16 grams of 2-ω-dihydroxy-*aa*-diphenylpropane in 100 c.c. of absolute alcohol is heated on a boiling-water bath, dry hydrogen chloride being passed through the solution at intervals. The solution is reduced to 20 c.c. and diluted with 300 c.c. of water, which causes a heavy oil to separate. The oil is extracted with ether, and the ethereal extract washed first with dilute alkali and then with water. The dried ethereal extract gives, on evaporation, an oil, which is dried in a vacuum over paraffin. The substance obtained in this way is very readily soluble in the usual organic solvents, but by dissolving about one part of the oil in about four parts of boiling light petroleum and keeping in a freezing mixture of ice and salt, long, prismatic needles are obtained, which melt sharply at 38·5°. The yield is 78 per cent. of the theoretical. The addition of ferric chloride to a suspension of 3-phenylchroman in concentrated sulphuric acid produces a reddish-violet coloration, even if the substance has been crystallised several times. Chroman, prepared according to Semmler's method (*loc. cit.*), and 1-phenylchroman also give a faint violet coloration with ferric chloride and concentrated sulphuric acid. These observations are of great interest in connexion with the chemistry of catechin, in view of the importance which has been attached to the fact that both catechin tetramethyl ether and the coumarans give a violet coloration with ferric chloride and concentrated sulphuric acid (compare Kostanecki and Lampe, *Ber.*, 1906, **39**, 4007; Freudenberg, *ibid.*, 1920, **53**, [*B*], 1423) (Found *: C = 86·1; H = 6·8. $C_{15}H_{14}O$ requires C = 85·7; H = 6·6 per cent.).

2-Hydroxy-aa-diphenylpropane (IV).

Nine grams of 3-phenylchroman, dissolved in 150 c.c. of alcohol, are heated with 40 grams of metallic sodium, and the alcohol is removed with steam. From the fact that, on steam distillation, no unchanged 3-phenylchroman was recovered, as observed in the case of 1-phenylchroman, it may be deduced that the 3-phenylchroman nucleus undergoes fission more easily than the 1-phenylchroman nucleus.

The ethereal extract of the acidified solution leaves, on evaporation, an oil, which gives a main fraction boiling at 226—231°/13—14 mm. The pure substance is a viscous, colourless oil, which boils at 214—216°/5—6 mm., and is soluble in all the usual organic solvents. The product does not solidify, even on prolonged

* Dried over paraffin in a vacuum.

keeping in a vacuum or in a freezing mixture. The alcoholic solution of 2-hydroxy-*aa*-diphenylpropane turns violet with alcoholic ferric chloride. The yield is 71 per cent. of the theoretical (Found *: C = 85·2; H = 7·8. $C_{15}H_{16}O$ requires C = 84·9; H = 7·5 per cent.).

Diazomethane converts the ethereal solution into the *methyl ether*, the yield being 74 per cent. of the theoretical. It is a viscous, colourless oil, which boils at 176—179°/4—5 mm. (Found *: C = 84·7; H = 8·1. $C_{16}H_{18}O$ requires C = 85·0; H = 7·9 per cent.).

2-Hydroxydiphenylacetic Acid (V).

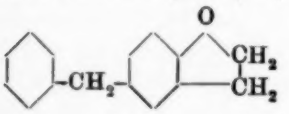
Five grams of 2-hydroxy-*aa*-diphenylpropane, dissolved in 100 c.c. of a 20 per cent. solution of potassium hydroxide in water, are oxidised on a boiling-water bath for four hours with 5 grams of potassium permanganate in 100 c.c. of water. The solution is filtered while hot, and, after cooling, acidified with dilute sulphuric acid. The grey-coloured precipitate is not filtered, but the solution extracted several times with ether, in which the precipitate dissolves. The dried ethereal extract leaves a solid, which crystallises from dilute alcohol, with the aid of animal charcoal, in prismatic needles melting at 86—87°, as given by Bistrzycki and Flatau (*Ber.*, 1895, **28**, 990). The yield is 64 per cent. of the theoretical.

On heating 2 grams of the acid with acetic anhydride and anhydrous sodium acetate, a quantitative yield of 2-phenylcoumaran-1-one is obtained (compare this vol., p. 1155). It crystallises from alcohol in prismatic needles, which melt at 113—114°, as given by Bistrzycki and Flatau (*loc. cit.*, p. 989).

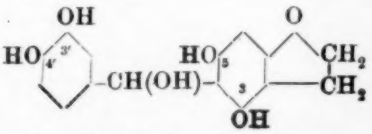
Neither the melting point of 2-hydroxydiphenylacetic acid nor of 2-phenylcoumaran-1-one was found to be depressed when mixed with the corresponding substances which had been prepared according to Bistrzycki and Flatau's method.

Addendum.

Marschalk (*Ber.*, 1910, **43**, 1700), at the suggestion of Kostanecki, has proposed the names depsan (from δέφω, to tan) for *p*-benzylcoumaran, depsanol for leuco-*p*-benzoylcoumaran, and 3 : 5 : 3′ : 4′-tetrahydroxydepsanol for catechin.



Depsan.



Catechin (Kostanecki's formula).

* Dried over paraffin in a vacuum.

This nomenclature has been freely used by Kostanecki's collaborators (compare, for example, Bielinki, *Diss.*, Bern, 1911), which is to be regretted, for the following reasons: (1) From Emil Fischer's well-known researches, the name depside, which is also derived from δέφω, has become definitely associated with a series of anhydrides. (2) The name tetrahydroxydepsanol, suggested for catechin, indicates that catechin possesses tanning properties, which is not the case (compare Procter, "The Principles of Leather Manufacture," 1903; Perkin and Everest, "The Natural Organic Colouring Matters," 1918). (3) Most of the recent researches point towards a chroman formula for catechin, as originally suggested by A. G. Perkin (T., 1902, **81**, 1172; 1905, **87**, 404), and the possibility that catechin is a coumaran derivative has become very remote.

For these reasons, the authors would suggest that the names depsan, depsanol, etc., should no longer be used in connexion with catechin.

The authors wish to express their indebtedness to the Colston Society of the University of Bristol for a grant which has covered the expenses of this research.

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CHEMICAL DEPARTMENT,
UNIVERSITY OF BRISTOL. [*Received, November 9th*, 1920.]

CLXXVIII.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part III.* 1 : 4-*Naphthylenebisiminocamphor.*

By BAWA KARTAR SINGH and MAHAN SINGH.

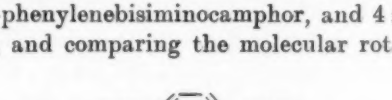
THE highest recorded molecular rotation is that of *p*-phenylenebisiminocamphor, which has $[M]_D$ 6173° in pyridine (Forster and Thornley, T., 1909, **95**, 942).

In the present communication is recorded the molecular rotatory power of another similarly constituted compound, namely, 1 : 4-*naphthylenebisiminocamphor*, which is endowed with a far higher rotatory power than any compound hitherto known.

The marked effect of conjugated linkings on the optical rotation of compounds has already been demonstrated by Rupe (*Annalen*, 1910, **369**, 311) and Hilditch (T., 1909, **95**, 1570). It is further

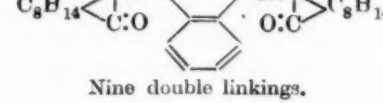
emphasised by the rotation-constants of a series of compounds, similar to the one under discussion, described by Forster (*loc. cit.*) and Singh (T., 1919, **115**, 19; this vol., p. 980) and their collaborators.

One of the necessary conditions for producing compounds of high molecular rotation appears to be to have within a relatively narrow molecular compass the optimum association of unsaturated groups. It is brought out very clearly by counting the number of double linkings in the structural formulæ of 1:4-naphthylenebisiminocamphor, *p*-phenylenebisiminocamphor, and 4:4′-diphenylenebisiminocamphor, and comparing the molecular rotatory powers in chloroform:



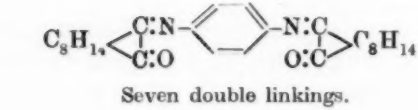
..... 8175°

Nine double linkings.



..... 6096°

Seven double linkings.



... 5360°

Ten double linkings.

This illustrates the effect of the optimum association of azethenoid groups, conjugated linkings, and benzene rings within a given molecular compass. The narrower the molecular compass containing a given number of conjugated linkings, the higher is the rotation.

The effect of solvent on the magnitude of rotation of 1:4-naphthylenebisiminocamphor is remarkable. It is shown in the following table:

	$[M]_D$.			
	Chloroform.	Methyl alcohol.	Ethyl alcohol.	Pyridine.
1:4-Naphthylenebisiminocamphor ...	8175°	9052°	12071°	13416°
p-Phenylenebisiminocamphor	6096 *	5009	5289	6173 *
Difference	2079	4043	6782	7243

* Forster and Thornley (*loc. cit.*).

Experimental.

1 : 4-*Naphthylenebisiminocamphor*.

When camphorquinone (2 mols.), 1 : 4-naphthylenediamine dihydrochloride (1 mol.), and excess of sodium acetate are thoroughly mixed, a red colour is developed almost immediately. The mixture, after being heated for half an hour on the water-bath at 60—70°, is extracted with alcohol, and, on diluting with water, a red substance is deposited, which crystallises from alcohol in red, rectangular plates melting at 228—229° (with blackening).

It is soluble in pyridine, chloroform, ethyl alcohol, or methyl alcohol, and insoluble in ether or water (Found: N = 6·33. $C_{30}H_{34}O_2N_2$ requires N = 6·16 per cent.).

The rotatory power determinations were made by dissolving the given weight of the substance in the given volume of the solvent, and the following results, without any mutarotation, were obtained. The length of the tube was 0·5-dcm. in the case of pyridine, and in the case of the remaining solvents it was 2-dcm.

Solvent.	Substance. Gram.	Volume. C.c.	Temperature.	α_D.	$[M]_D$.
Chloroform	0·0213	40	18·1°	1·914°	8157°
,,	0·0186	100	18·8	0·668	8196
Methyl alcohol	0·0181	100	18·4	0·732	9052
Ethyl alcohol	0·0132	100	18·4	0·706	12071
,,	0·0168	100	18·4	0·905	12239
Pyridine	0·0122	50	30	0·36	13416

All attempts to reduce this compound have failed.

For comparison with the foregoing substance, the following measurements were made with *p*-phenylenebisiminocamphor:

Solvent.	Substance. Gram.	Volume. C.c.	Temperature.	α_D.	$[M]_D$.
Chloroform	0·0286	20	24·5°	4·31°	6088
Methyl alcohol	0·0357	20	21·7	4·41	5009
,,	0·0254	20	21·7	3·15	5005
Ethyl alcohol	0·0264	20	21·7	3·46	5289

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[*Received, November 9th*, 1920.]

CLXXIX.—*The Permeability of Glass to Iodine and Bromine Vapours.*

By James Brierley Firth.

In a previous communication (P., 1913, **29**, 112) the author described experiments which showed that ordinary glass is not permeable to the vapours of iodine and bromine at 360° after fifty days, and after two years at the ordinary temperature.

In the present paper, the results are recorded after the experiments have been continued for a further period of seven and a-half years, making nine and a-half years in all.

After two years, the tubes of the second series were again heated for a further period of fifty days at 360°, and then the tubes of both series set aside and examined periodically.

After a period of nine and a-half years, the silver in the tubes of the first series, namely, those which had not been heated, showed no indication of attack by the halogen, but in the case of the tubes which had been heated to 360° (100 days in all), the silver in two of the tubes showed distinct attack in the case of iodine, whilst in the case of bromine, in this series also, there was no indication of any action on the silver.

The tubes were then broken up, and the thickness of the walls of the bulbs was accurately measured by means of a micrometer gauge. The silver foil in every case was carefully examined, and the presence of silver iodide confirmed in the two cases.

The measurement of the thinnest part of the bulb is given in each case.

In the first series, the thickness of the bulbs varied in the case of bromine from 0·206 to 0·332 mm., and in the case of iodine from 0·204 to 0·338 mm.

In the second series, the thickness varied from 0·207 to 0·364 mm. in the case of bromine and 0·208 to 0·385 mm. in the case of iodine.

In the tubes in which the silver was attacked by iodine, the thicknesses of the bulbs containing the halogen were 0·208 mm. and 0·211 mm. respectively, and the conditions (*a*) vacuum inside and outside, (*b*) vacuum outside and atmospheric pressure inside, at the ordinary temperature.

It should be noted that in the case of the tubes which had been heated, the iodine condensed on the walls of the bulb as a thin film, whereas in the case of the tubes which had not been heated, the iodine was in small crystals.

The experiments indicate that it is possible for iodine to pass through a thin glass partition under certain conditions, but the rate of diffusion is exceedingly slow, the iodine taking about nine years to diffuse through a thickness of 0·2 mm. of glass. There is no evidence whatever of the passage of bromine through a similar thickness of glass, even after nine and a-half years.

The experiments do not in any sense support the explanation of Zengelis for the loss observed in Landolt's experiments, since the time taken in the cases where a positive result has been obtained is considerably greater than the duration of Landolt's experiments, and, further, the thickness of the glass penetrated would be much less than the thickness of the glass used by Landolt.

In conclusion, therefore, it may be stated that iodine and bromine do not diffuse through a glass partition under ordinary experimental conditions, but only in extreme cases, involving the use of very thin glass over a very long period, does the possibility arise.

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[*Received, November 16th*, 1920.]

CLXXX.—*The Velocity of Decomposition of High Explosives in a Vacuum. Part II. Trinitrophenylmethylnitroamine (Tetryl).*

By ROBERT CROSBIE FARMER.

TETRYL is widely used for explosive purposes, and the control of its stability is of considerable practical importance. On account of the instability of the nitroamino-group, the compound decomposes much more rapidly than compounds of the trinitrobenzene type, and may undergo deterioration on storage if not completely purified. It was mainly for the control of the manufacture of tetryl that the vacuum stability test described by the author (this vol., p. 1432) was devised, and this test has been used as the standard method for a number of years.

A temperature of 120° has been found best for the measurements. Tetryl is solid at this temperature (m. p. 129°), and gives convenient volumes of gas in about two days. The gases consist of carbon dioxide, carbon monoxide, nitrogen, and oxygen, and the residue is a complex mixture containing picric acid, etc. The

evolution of gas proceeds with an acceleration, and an arbitrary period of forty hours has been taken for the standard test. Samples of well-purified tetryl give evolutions of 1·5 to 3 c.c. from 5 grams of explosive. The reaction is very sensitive to catalytic influences, and products containing minute quantities of residual impurities decompose much more rapidly. It appears probable that one of the main causes of instability is the presence of analogues of tetryl containing a nitro-group in the meta-position. Traces of picric acid may also be present; this compound has been found to decrease the stability greatly.

The temperature-coefficient corresponds with a factor of 1·9 for each 5°, that is, approximately the same as for most other explosives which undergo gradual decomposition. The logarithms of the velocities give approximately a straight line when plotted against the temperatures. By extrapolation to ordinary temperature, it is found that forty hours at 120° corresponds with about 1700 years at 20°. Such extrapolations must naturally be taken with reserve, as the decomposition is of a complex nature, and may include reactions the temperature-coefficients of which vary, but the result shows that the purified substance is almost free from any tendency to decompose when stored at ordinary temperatures, unless decomposition is induced by contact with any material of a reactive nature.

A point of interest in the study of the stability of tetryl is that measurements can be made both above and below the melting point. In the case of most nitro-compounds, the velocity of decomposition becomes so low at the melting point that measurements on the solid compound are scarcely possible. In view of the behaviour of many substances of melting with simultaneous decomposition, it is instructive to make quantitative tests in the solid and the molten condition. When measurements are made on the solid substance at different temperatures, a uniform temperature-coefficient is obtained. At the melting point, an abrupt change takes place in the velocity of decomposition. The effect of the molten condition is to increase the velocity approximately fifty-fold. Beyond this point, the velocity again increases uniformly with the temperature, as before. When the logarithms of the velocities are plotted against the temperature, the measurements above the melting point give a straight line, which is approximately parallel to the line representing the velocities below the melting point (Fig. 5).

This great increase of velocity on melting is the main cause of the acceleration in the decomposition at 120°. When a slight decomposition has occurred, the products of the decomposition

form a eutectic mixture with a part of the tetryl, and this liquid portion at once decomposes with the higher velocity. It is always observed after testing that the crystals show signs of having been partly melted. This acceleration tends to accentuate the difference between tetryls of different initial stability. In the molten condition the acceleration is much less marked, and is in this case due to auto-catalysis. Pure and impure samples also show much less difference in their velocity curves in the molten condition.

The rapid decomposition of molten tetryl makes it impossible to obtain accurate measurements of its freezing point ("setting point"), but the melting point can be determined by the capillary method without any appreciable error due to decomposition. The purest samples gave a melting point of 129·1°.

The above behaviour on melting formed an explanation of the results obtained on mixing tetryl with trinitrobenzene, trinitrotoluene, etc. These mixtures decomposed much more rapidly than tetryl itself at 100° to 120°. This appeared at first to indicate a chemical interaction, but was simply due to the lowering of the melting point of the tetryl. The rates of decomposition of the mixtures at temperatures above the melting point of tetryl agreed with those of tetryl, whilst at lower temperatures they agreed with the extrapolated velocities from the temperature–velocity curve of molten tetryl (Fig. 5). It may therefore be concluded that at temperatures below the melting point of the eutectic mixtures the stability of these mixtures will not differ from that of tetryl alone. It was not possible to test this, as the rate of decomposition of tetryl can scarcely be measured at temperatures much below 100°. In the case of *s*-trinitro-*m*-xylene, however, it was possible to obtain measurements below the melting point of the eutectic mixture, and these agreed approximately with those made on tetryl alone. These deductions have been confirmed by prolonged climatic trials of such mixtures at 50°.

Trinitrophenol caused a great increase in the rate of decomposition of tetryl, after making allowance for the lowering of the melting point. As trinitrophenol is a decomposition product of tetryl, this probably forms the main explanation of the auto-catalysis.

Mixtures of small proportions of nitric and acetic acid did not accelerate the decomposition. Probably the acids were removed by distillation in the vacuum before they were able to exert any decomposing action. Sulphuric acid, on the other hand, gave rise to a very rapid evolution of gas.

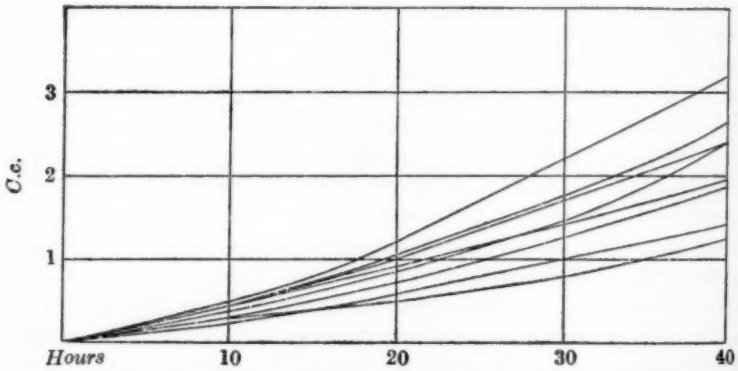
Since the completion of the above work, a few measurements have been given by Knowles (*J. Ind. Eng. Chem.*, 1920, **12**, 246),

using a modification of Obermüller's test. He gives the gas evolution as 20 to 30 mm. per hour for commercial tetryls, but the temperature and the volume of the apparatus are not stated.

Experimental.

Method of Working.—This was essentially the same as that described in Part I (*loc. cit.*). The standard procedure was as follows: The tetryl was dried for four hours in a steam-oven, and 5 grams were weighed into the heating tube, which was then connected with the manometer. A mixture of heavy petroleum and ceresine wax was used as lubricant; these ingredients were carefully examined to ensure that they were inert, and the smallest possible quantity of the lubricant was used. After exhaustion,

Fig. 1.



Normal decomposition of tetryls as manufactured (5 grams at 120°).

the tube was heated for a few hours at 80° to remove any volatile matter, and was then again exhausted and flushed out twice with dry air. The exhausted tube was then inserted in the bath at 120°, and packed round the top with asbestos wool. A period of one and a-half hours was allowed for the level of the mercury in the manometer to become steady, and readings were then taken over a period of forty hours. For special purposes, such as the measurement of temperature-coefficients, the above conditions were modified as required. Precautions against explosion were taken as described in Part I, but no explosion of tetryl occurred in the whole of the experiments.

(a) *Typical Results of Tetryl as Manufactured and Purified by Acetone and Water.*—A number of these is shown in Fig. 1. The

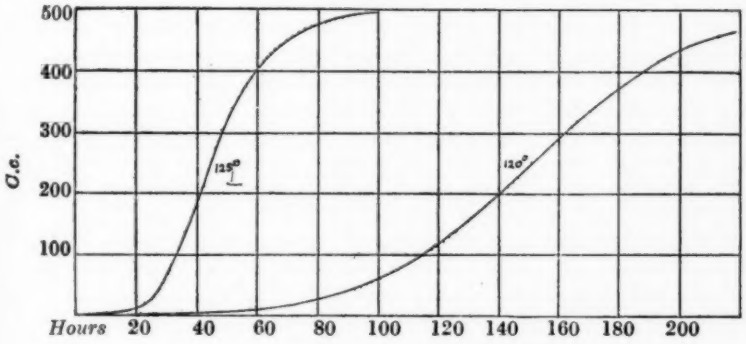
general character of the evolution is seen from the curves. A marked acceleration occurs, due in part to auto-catalysis, but in a greater degree to the progressive formation of eutectics. Attempts to determine the order of reaction serve, therefore, no useful purpose.

Analysis of the gases from three experiments gave the following results:

	(i.)	(ii.)	(iii.)
CO_2	20·0	21·5	23·3
CO	5·5	7·1	5·8
O_2	6·9	6·1	4·9
N_2	67·6	65·3	66·0

These analyses do not take account of the nitric peroxide present. This was determined spectroscopically, as indicated in experiments cited below.

FIG. 2.



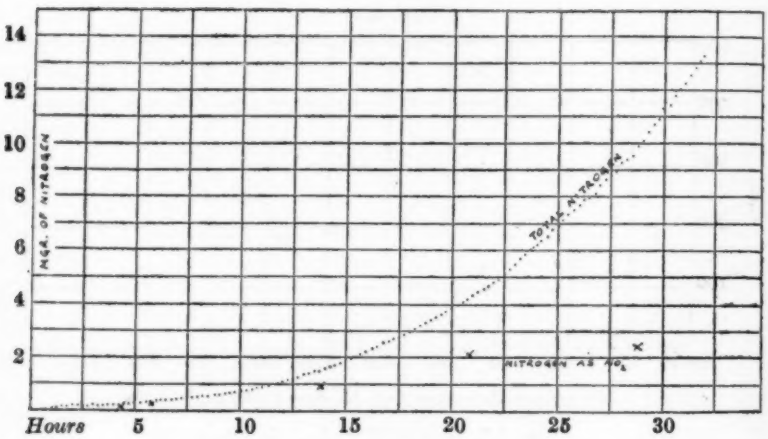
Prolonged decomposition (*5 grams of tetryl*).

(b) *Decomposition in Air and in a Current of Carbon Dioxide.*—The velocity of evolution of gas at atmospheric pressure was originally used for the comparison of the stability of samples of tetryl, but although this formed some guide in the purification of tetryl during the manufacture, it was not so trustworthy as the vacuum method, and may therefore be passed over. Two experiments may, however, be quoted in which the decomposition at atmospheric pressure was continued until the gas-evolution almost ceased. The object of these was to ascertain whether the acceleration which occurred at first would continue until it culminated in an explosion. The thermostat was surrounded by a mound of earth, and the readings were taken with a telescope. No explosion occurred, however, and it was possible to observe the whole course of the gas-evolution. Fig. 2 shows the gas-evolution from 5 grams of tetryl at 120° and 125° respectively. In the latter case, the

gas-evolution ultimately almost ceased, and the total volume of gas amounted to 1·27 mols. per mol. of tetryl. The residue was a dark, resinous mass, which did not yield any results on crystallisation.

Will's method (*Zeitsch. angew. Chem.*, 1901, **14**, 743, 774), in which the explosive is heated in a current of carbon dioxide, was also applied to tetryl. Fig. 3 shows the evolution of nitrogen from 2·5 grams of tetryl at 125° over a period of thirty-two hours. The proportion of nitric peroxide was also measured spectroscopically by Robertson and Napper's method (T., 1907, **91**, 761). On account of the low rate of evolution, a very long observation tube was necessary in order to render the spectrum of the nitric peroxide

FIG. 3.



Will test (2·5 *grams of tetryl at* 125°).

distinctly visible. The proportion of nitric peroxide decreased as the evolution proceeded (Fig. 3).

It is of interest to compare the evolution of nitrogen from tetryl and guncotton, respectively, under the conditions of Will's test. A good guncotton gives approximately 1·5 milligrams of nitrogen in four hours at 125° in a current of carbon dioxide, whereas tetryl, when well purified, gives only 0·15 to 0·21 milligram in four hours. Its rate of decomposition is therefore only about one-tenth that of guncotton.

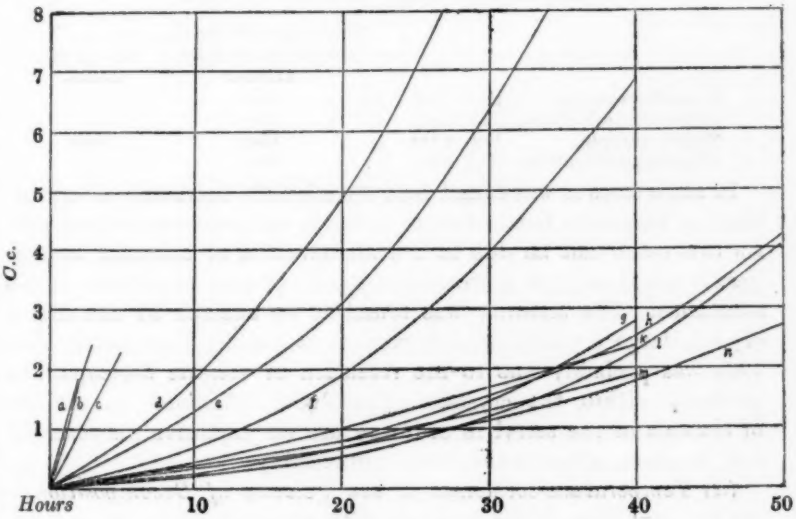
(c) *Purification of Tetryl.*—The application of the vacuum test to the control of stability in the purification treatment is illustrated in the following examples. Fig. 4 shows the effect of fractional precipitation of crude tetryl from acetone by water, after

removing the nitration acids by treatment with hot water. The bulk of the tetryl was contained in fraction 2, which showed the greatest stability.

Gas-evolution from 5 Grams at 120°.

		Time required for evolution of 2 c.c. Hours.	C.c. in 40 hours.
Undissolved residue,	Fig. 4 (*c*)	4·5	—
First precipitation,	Fig. 4 (*e*)	14·5	11·80
Second ,,	Fig. 4 (*k*)	34·0	2·40
Final ,,	Fig. 4 (*a*)	2·5	—

FIG. 4.



Purification of tetryl.

This was confirmed by the Will test, which gave the following evolutions of nitrogen from 2·5 grams of tetryl in four hours at 125°: undissolved residue, 3·39; crop 1, 0·51; crop 2, 0·16; final crop, 5·76 milligrams.

Re-purification of the tailings by the same method gave the following results:

Crop 1 (5 grams),	Fig. 4 (*m*)	...	1·90 c.c. in 40 hours.
Crop 2 (5 grams),	Fig. 4 (*h*)	...	2·55 c.c. ,,
Residue (5 grams),	Fig. 4 (*n*)	...	1·80 c.c. ,,

A stable crop of crystals from the acetone–water treatment was

further crystallised from alcohol, but this did not decrease the rate of decomposition.

Before crystallisation from alcohol	2·40 c.c.	in 40 hours,	Fig. 4 (*k*)
After	„	„	„	2·80 c.c.	„	„	„	Fig. 4 (*g*)

In order to ascertain whether tetryl which had been partly decomposed could be restored to its original stability by crystallisation, the residue from a test after forty-four hours at 120° was recrystallised from alcohol. This gave 6·85 c.c. from 5 grams in forty hours at 120°, showing that the harmful impurities had not been removed (Fig. 4, *f*).

Crystallisation from toluene was applied to a very impure sample and to a sample previously purified by acetone and water.

Gas-evolution from 5 Grams at 120°.

			Time required for an evolution of 2 c.c. Hours.	C.c. in 40 hours.
Unstable sample,	Fig. 4 (*b*)	...	2·5	—
After crystallisation,	Fig. 4 (*d*)	...	10·5	—
Stable sample,	Fig. 4 (*k*)	...	34·0	2·40
After crystallisation,	Fig. 4 (*l*)	...	37·0	2·30

In some cases it was found that the stability decreased on crystallisation, especially from solvents in which tetryl was readily soluble. As this could not be due to the introduction of chemical impurities, it could only be attributable to the physical condition of the substance. The stability was found to be affected by the size of crystal, large crystals decomposing more rapidly than small ones. This was probably due to the retention of volatile decomposition products within the crystals. The slight differences in the size of crystals of the tetryl in ordinary use for explosive purposes did not, however, affect the stability appreciably.

(d) *Temperature-coefficient of the Velocity of Decomposition.*—As the evolution of gas proceeds with an acceleration, it was con-

Influence of Temperature on Rate of Decomposition.

Tetryl Grams.	Temperature.	Time (hours) for evolution of 0·5 c.c.	1·0 c.c.	2·0 c.c.	5·0 c.c.	Initial velocity. C.c. per gram per hour.	Log.
5·0	100·0°	141	—	644	—	0·00071	$\bar{4}$·85
5·0	100·0	164	—	—	—	0·00061	$\bar{4}$·79
5·0	111·0	—	73	152	255	0·0027	$\bar{3}$·43
5·0	111·0	—	69	147	253	0·0029	$\bar{3}$·46
5·0	120·0	—	26	42	65	0·0077	$\bar{3}$·89
5·0	120·0	—	23	37	—	0·0087	$\bar{3}$·94
0·5	126·8	6·0	7·3	—	—	0·10	$\bar{1}$·00
0·5	129·9	—	1·35	2·2	4·4	1·5	0·18
0·5	134·6	—	0·56	1·09	2·42	3·6	0·56
0·5	135·3	—	0·42	0·78	1·66	4·8	0·68
0·5	138·6	—	0·27	0·53	1·19	7·4	0·87

sidered best to take the initial velocities as the basis for the calculation of the temperature-coefficient. Measurements were made both above and below the melting point.

The lower curve in Fig. 5 shows the logarithms of the velocities in relation to the temperature. It is seen that the solid substance has a regular temperature-coefficient (approximately equal to 1·9 for 5°). At the melting point there is a break in the curve, and above this point it again proceeds in a straight line. The measurement at 126·8 gave a low velocity at the start, but this increased extremely rapidly as the tetryl melted. The difference in velocity between solid and molten tetryl at 120° is in the ratio of 1 to 50.

The following table shows the effect of heating mixtures of tetryl with trinitrotoluene and other nitro-compounds.

Mixtures of Tetryl with Nitro-compounds.

Influence of Temperature.

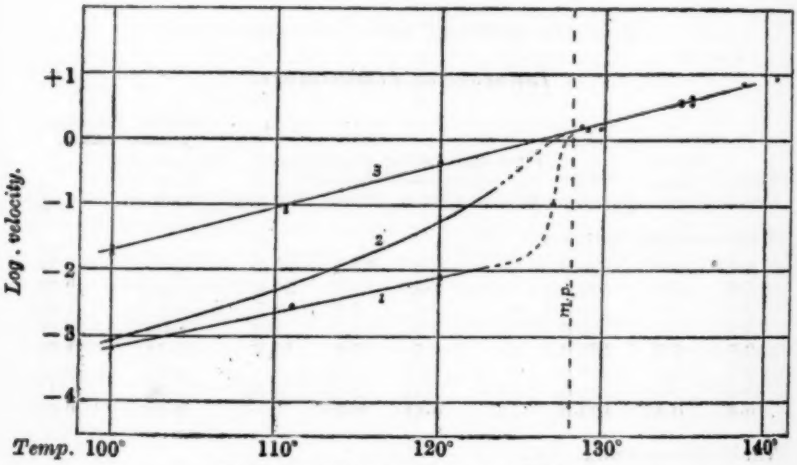
Tetryl. Grams.	Admixture. Grams.	Temperature.	Time (hours) for evolution of 0·5 c.c.	1·0 c.c.	2·0 c.c.	5·0 c.c.	Initial velocity. C.c. per gram of tetryl per hour.	Log.
Trinitrotoluene mixtures :								
5·0	5·0	100·0°	—	8·5	14·3	28·7	0·023	$\bar{2}$·36
5·0	5·0	100·0	—	8·5	14·7	30·4	0·023	$\bar{2}$·36
5·0	5·0	110·5	—	2·6	4·4	8·5	0·077	$\bar{2}$·89
5·0	5·0	110·6	—	2·5	4·3	8·3	0·080	$\bar{2}$·90
0·5	0·5	120·0	—	4·5	7·8	14·8	0·44	$\bar{1}$·64
0·5	0·5	128·6	—	1·23	2·23	—	1·63	0·21
0·5	0·5	129·0	—	1·41	2·48	4·85	1·42	0·15
0·5	0·5	134·6	—	0·51	0·90	—	3·92	0·59
Trinitrobenzene mixtures :								
5·0	2·5	100·0	—	10·4	17·4	35·0	0·019	$\bar{2}$·28
5·0	5·0	110·5	—	2·4	3·95	—	0·083	$\bar{2}$·92
5·0	5·0	110·6	—	2·5	3·92	—	0·080	$\bar{2}$·90
0·5	0·5	1[illegible]·0	—	4·05	6·40	13·2	0·49	$\bar{1}$·69
0·5	0·5	135·3	—	0·56	1·00	2·18	3·57	0·55
Trinitroxylene mixtures :								
5·0	2·5	100·0	124·0	—	—	—	0·00081	$\bar{4}$·91
5·0	2·5	110·0	21·5	36·7	61·5	99·0	0·0047	$\bar{3}$·67
5·0	2·5	120·0	1·86	—	—	—	0·054	$\bar{2}$·73
0·5	0·5	140·7	—	0·24	0·43	0·99	8·3	0·92
0·5	0·5	140·8	—	0·20	0·38	0·85	10·0	1·00
Dinitrobenzene mixtures :								
5·0	5·0	100·0	—	11·1	16·8	29·9	0·018	$\bar{2}$·26
5·0	5·0	100·0	—	12·0	18·3	31·8	0·017	$\bar{2}$·23

Fig. 5 shows the relationship between the logarithms of the velocities and the temperature. It is seen that above the melt-

ing point of tetryl (129°) the velocities for tetryl and the mixtures coincide. Below 129° the values for solid tetryl are much lower (curve 1). The values for the mixtures with dinitrobenzene, trinitrobenzene, and trinitrotoluene are shown in curve 3. These admixtures lower the melting point of the tetryl and form liquid mixtures; the velocities of decomposition correspond, therefore, with those of molten tetryl, and their logarithms lie approximately on a straight line forming an extrapolation of the values for molten tetryl.

In the case of trinitroxylene, the eutectic is almost completely solid at 100°, and here the velocity becomes nearly equal to that of solid tetryl (curve 2). Measurements on the trinitrotoluene and

FIG. 5.



Influence of temperature on velocity.

trinitrobenzene mixtures were not taken below the eutectic melting points, but prolonged climatic trials at 50° indicated that very little decomposition occurred in a year at this temperature.

A noticeable feature of the mixtures of tetryl with trinitrobenzene (and to a less extent with trinitrotoluene) was that, on cooling to the ordinary temperature after melting, they remained very persistently supercooled, forming viscous, dark, reddish-brown colloids. The trinitrobenzene mixtures crystallised only after several days.

Various tetryls were mixed with trinitrotoluene to ascertain whether tests at 100° would be of value in discriminating between pure and impure samples. This method was, however, of relatively little value as compared with the direct test on solid tetryl at 120°.

In all cases, the acceleration of the decomposition is much greater in the solid condition, in consequence of the progressive melting due to the decomposition. This is shown in the following table.

Acceleration in the Decomposition of Tetryl.

	Tetryl. Grams.	Temperature.	Initial velocity.	Mean velocity from 2 c.c. to 5 c.c.	Ratio.
Solid	5·0	111·0°	0·0027	0·0058	2·1
„	5·0	111·0	0·0029	0·0057	2·0
„	5·0	120·0	0·0077	0·026	3·4
Liquid.....	0·5	129·9	1·5	2·7	1·8
„	0·5	134·6	3·6	4·5	1·3
„	0·5	135·3	4·8	6·8	1·4
„	0·5	138·6	7·4	9·1	1·2

This was confirmed by the Will test in a current of carbon dioxide. Thus the values at 125° were as follows:

First	4 hours :	0·21 milligram of N_2 per 2·5 grams of tetryl.
Second	„ „	0·53 „ „ „ „
Third	„ „	2·25 milligrams „ „ „
Fourth	„ „	6·28 „ „ „ „
Fifth	„ „	13·39 „ „ „ „

(e) *Reactions of Tetryl.*—Nitric and acetic acids in small proportion did not affect the velocity of evolution materially. In general, acids accelerate the decomposition, but these acids, being volatile, were probably removed by the vacuum before they had time to exert any catalytic action.

Gas-evolution at 120°.

	20 hours.	40 hours.
Tetryl, 5 grams	0·95	2·70
Tetryl, 5 grams Nitric acid, 0·01 gram }	0·85	2·38
Tetryl, 5 grams Acetic acid, 0·01 gram }	0·83	2·33

Sulphuric acid, on the other hand, being non-volatile, accelerated the decomposition very greatly. Even at 80° a marked evolution of gas occurred.

Gas-evolution at 80°.

	20 hours.	40 hours.	60 hours.	80 hours	100 hours.
Tetryl, 5 grams Sulphuric acid, 0·01 gram }	1·60	2·70	3·55	4·15	4·45

Picric acid also gave rise to a rapid evolution of gas when mixed with tetryl.

	Temperature.	½ hour.	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
Tetryl, 5 grams	120°	—	0·50	1·25	3·50	8·50	—
„ „	100	—	0·15	0·20	0·25	0·30	0·35
Tetryl ... 4·5 grams / Picric acid 0·5 gram ...	120	0·85	—	—	—	—	—
„ „ „ „ ...	100	—	1·60	3·90	6·40	9·20	12·35
„ „ „ „ ...	60	—	—	—	—	—	0·02

Some allowance must be made for partial melting of the tetryl containing 10 per cent. of picric acid, but, apart from this, the picric acid certainly affected the stability adversely. Picric acid was found to be a decomposition product of tetryl, and this is doubtless one of the causes of the auto-catalysis which is observed.

The influence of some other admixtures is shown in the following table. These all formed liquid mixtures with tetryl at 100°, and, on this account, the velocities should be compared with that of a mixture of tetryl and trinitrotoluene rather than tetryl alone. In the case of *p*-dichlorobenzene, the liquefaction was probably incomplete.

Gas-evolution at 100°.

	Hours required for evolution of 1 c.c.	2 c.c.	3 c.c.	Initial velocity. C.c. per gram of tetryl per hour.
Tetryl 5 grams / Nitrobenzene 5 „	5·6 / 6·8	9·0 / 10·3	17·1 / 18·6	0·036 / 0·029
Tetryl 5 „ / *p*-Dichlorobenzene 5 „	17·0	25·0	42·0	0·012
Tetryl 5 „ / Diphenyl ether 5 „	2·7	5·1	—	0·074

Summary.

The velocity of evolution of gas in a vacuum at 120° forms a useful method for the control of the stability of tetryl in the manufacture. The effect of purification and of various admixtures is shown. The temperature-coefficient of the decomposition of solid tetryl is 1·9 for 5°. At the melting point, an abrupt change in the velocity is observed, the molten tetryl decomposing about fifty times as rapidly as the solid. The acceleration in the decomposition of tetryl at 120° is to a great extent due to progressive melting. Admixtures which lower the melting point also give a rapid evolution, apart from any chemical action which they may exert.

The thanks of the author are due to the Director of Artillery for permission to publish the above results.

RESEARCH DEPARTMENT,
ROYAL ARSENAL,
WOOLWICH.

[*Received, November 13th*, 1920.]

CLXXXI.—*The Formation of* 2:3:6-*Trinitrotoluene in the Nitration of Toluene.*

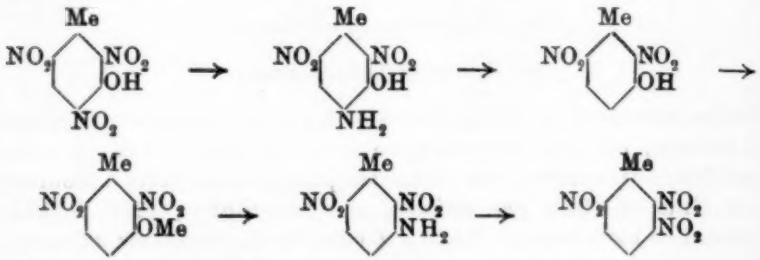
By Royston Barry Drew.

In the mixture of trinitrotoluenes obtained by the direct nitration of toluene, previous workers have identified only 2:4:6-, 2:3:4-, and 3:4:6-trinitrotoluenes of the six possible isomerides. Molinari and Giua (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1914, **9**, 239) claimed to have isolated the 2:3:6-compound, previously unknown, to which they assigned a melting point of 79·5°, but this compound has been synthesised by Körner and Contardi (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339) and by Brady and Taylor (this vol., p. 876), and found to melt at 111°; the latter authors have suggested that Molinari and Giua's compound was probably a molecular compound of 2:3:4- and 3:4:6-trinitrotoluenes. Will (*Ber.*, 1914, **47**, 704) has studied the nitration of 2:3- and 3:6-dinitrotoluenes, and states that the sole products of their nitration are 2:3:4- and 3:4:6-trinitrotoluenes. More recently, however, Marqueyrol, Koehler, and Jovinet (*Bull. Soc. chim.*, 1920, [iv], **27**, 420) have obtained a third trinitrotoluene, in addition to the 2:3:4- and 3:4:6-compounds, from the nitration of *m*-nitrotoluene. Their results are incomplete, and they have not identified the compound, but, as they found it was formed to a small amount in the nitration of 2:3- and 2:5-(or 3:6-)dinitrotoluenes, they conclude it must be either the 2:3:6- or the 2:3:5-trinitro-derivative. The present author, previous to the publication of Marqueyrol, Koehler, and Jovinet's results, had investigated the nitration of 2:3- and 3:6-dinitrotoluenes, and found that in each case the product contains about 15 per cent. of 2:3:6-trinitrotoluene.

Other workers have shown that about 4 per cent. of *m*-nitrotoluene is formed in the mono-nitration of toluene under the usual conditions, and that, on further nitration of this compound, about half the product is a mixture of 2:3- and 2:5-dinitrotoluenes. In crude trinitrotoluene, obtained by the direct nitration of toluene, there must be, therefore, about 0·3 per cent. of 2:3:6-trinitrotoluene. Opportunity, however, has not arisen to isolate this small amount from commercial samples of trinitrotoluene.

Further, a new method of preparing 2:3:6-trinitrotoluene has been devised, which is easier than that described by Körner and Contardi (*loc. cit.*), and starts from trinitro-*m*-cresol; this is more

readily obtainable than the 2:6-dinitrotoluene required in Brady and Taylor's synthesis (*loc. cit.*). The reactions involved are as follows:



Methylpicramic acid, obtained by the reduction of trinitro-*m*-cresol, has been oriented only indirectly by Borsche and Heyde (*Ber.*, 1906, **39**, 4092), and the above synthesis fully confirms the view of these authors.

Experimental.

Nitration of 3:6-*Dinitrotoluene*.—Forty grams of 3:6-dinitrotoluene were added to 250 c.c. of a mixture of sulphuric and nitric acids (HNO_3=17·5; H_2SO_4=78; H_2O=4·5 per cent.). The mixture was mechanically stirred, and the temperature raised to 80° and kept at that point for an hour, when the temperature was raised to 100° for a further two hours, and finally to 120° for fifteen minutes. The mixture was then cooled and poured into water, the solid collected, and washed repeatedly under water with the injection of steam until free from acid.

The freezing point of the product after drying was found to be 95·4°, as against 103° for pure 3:4:6-trinitrotoluene. The mixture was recrystallised from acetic acid to remove most of the 3:4:6-trinitrotoluene, and, by diluting the filtrate, a mixture richer in 2:3:6-trinitrotoluene was obtained. Attempts were made to separate this mixture by crystallisation from various solvents, but without success, a mixture melting constantly at 78° being obtained. A portion was treated with alcoholic ammonia in the hope that it would be possible to separate the corresponding dinitrotoluidines, but an oily, intractable product was obtained. A successful separation was ultimately brought about by the action of hydrazine hydrate. It had been observed by Brady (*private communication*) that hydrazine hydrate reacts readily with 2:3:4- and 3:4:6-trinitrotoluenes, giving red, crystalline compounds sparingly soluble in alcohol. It has been found that 2:3:6-trinitrotoluene behaves in a different manner towards this reagent,

which can therefore be used to effect a separation. The mixture of 3:4:6- and 2:3:6-trinitrotoluenes was dissolved in methyl alcohol, a solution of hydrazine hydrate added, and the mixture warmed on the water-bath for some time. On cooling, the red precipitate was collected and fractionally crystallised from alcohol, and from the more readily soluble portion a colourless compound was isolated, which was identified as 2:3:6-trinitrotoluene by the method of mixed melting points with a sample of this compound prepared by Brady and Taylor's method.

Nitration of 2:3-*Dinitrotoluene.*—This was effected in an exactly similar manner to the nitration of 2:6-dinitrotoluene. The product had a freezing point of 100°, as compared with 112° in the case of pure 2:3:4-trinitrotoluene. The separation was brought about by means of hydrazine hydrate, and the 2:3:6-trinitrotoluene isolated and identified. The approximate amount of 2:3:6-trinitrotoluene present in the mixtures obtained by the nitration of 3:6- and 2:3-dinitrotoluenes was determined by making up mixtures of pure 3:4:6- and 2:3:4-trinitrotoluenes with 2:3:6-trinitrotoluene, and determining their freezing points. It was found that these corresponded with the freezing points of the products of nitration when about 15 per cent. of the 2:3:6-compound was present.

2:6-*Dinitro*-m-*cresol.*—This was prepared from 2:6-dinitro-4-amino-*m*-cresol. The method given for the preparation of this compound by Kellner and Beilstein (*Annalen*, 1863, **128**, 166) did not give good yields, so a modified method was adopted. Twenty grams of trinitro-*m*-cresol were dissolved in 50 c.c. of boiling methyl alcohol, and 200 c.c. of 15 per cent. ammonium sulphide slowly added. Vigorous action took place, and, when it subsided, the mixture was cooled, diluted, and acidified with hydrochloric acid. The sulphur was filtered off, and the filtrate evaporated to small bulk. On keeping, the 2:6-dinitro-4-amino-*m*-cresol separated, and was crystallised from alcohol with the addition of animal charcoal. It was found that the usual method for the removal of the amino-group by the action of sodium nitrite on a boiling alcoholic solution of the amine containing sulphuric acid did not give good results with this compound, owing to the stability of the diazo-compound formed; accordingly, the following method was adopted.

Ten grams of 2:6-dinitro-4-amino-*m*-cresol were dissolved in 70 c.c. of hot alcohol, 20 c.c. of concentrated hydrochloric acid added, and then, gradually, 10 grams of sodium nitrite dissolved in a minimum amount of water. As soon as the reaction ceased, the mixture was cooled and the precipitate collected. There was

thus obtained a stable, greenish-yellow, crystalline material, which deflagrated on heating, and was probably the diazo-oxide corresponding with that obtained from picramic acid. This compound was treated with 30 c.c. of concentrated formic acid, and a small quantity of copper powder added, when a violent reaction took place, nitrogen and carbon dioxide being evolved. After filtering from the copper and diluting the filtrate, an oil separated, which slowly crystallised; the crystals were pressed on a porous tile and recrystallised from benzene, when 2:6-*dinitro*-m-*cresol* separated as a white, crystalline compound melting at 133° (Found: N = 14·1. $C_7H_6O_5N_2$ requires N = 14·1 per cent.).

2:6-*Dinitro*-m-*tolyl Methyl Ether*.—The ammonium salt of 2:6-dinitro-*m*-cresol was prepared by dissolving the cresol in alcoholic ammonia and evaporating the solution on the water-bath until crystallisation took place on cooling. The filtered crystals were dissolved in the minimum amount of alcohol, and the calculated quantity of alcoholic silver nitrate was added, when the silver salt separated in lustrous, grey crystals, which deflagrate violently on heating. Five grams of the silver salt were added to a solution of 5 c.c. of methyl iodide in alcohol, when immediate action took place, and, after removal of the silver iodide, the solution was diluted and the precipitated 2:6-*dinitro*-m-*tolyl methyl ether* crystallised from alcohol, when it was obtained in white needles melting at 115° (Found: N = 13·4. $C_8H_8O_5N_2$ requires N = 13·2 per cent.).

2:6-*Dinitro*-m-*toluidine and* 2:3:6-*Trinitrotoluene*.—Five grams of 2:6-dinitro-*m*-tolyl methyl ether were heated to 130° with 5 c.c. of ammonia and 20 c.c. of alcohol. On cooling and diluting, 2:6-dinitro-*m*-toluidine was precipitated, and identified by the method of mixed melting points with a sample of this compound prepared by Cook and Brady (this vol., p. 750). 2:6-Dinitro-*m*-toluidine can be converted into 2:3:6-trinitrotoluene by Körner and Contardi's method (*loc. cit.*).

The author wishes to express his thanks to the Director of Artillery for permission to publish this work.

RESEARCH DEPARTMENT,
ROYAL ARSENAL, WOOLWICH. [*Received, October 26th*, 1920.]

CLXXXII.—*Hyenanchin and other Constituents of* Hyenanche globosa.

By Thomas Anderson Henry.

Hyenanche globosa, Lamb (*Toxicodendron capense*, Thun), is the sole member of a genus of the natural order Euphorbiaceæ, and in distribution is confined to South Africa. The name of the plant is said to have originated from the use of the seeds in South Africa as a poison for wild animals, especially hyenas.

In 1858 Henkel obtained, by fractionation of a concentrated alcoholic extract of the fruits, a syrupy preparation, which proved to be highly toxic (*Arch. Pharm.*, 1858, **144**, 16). Engelhardt subsequently prepared the toxic constituent, which he named hyenanchin, in a crystalline condition, but, beyond stating that it was neither an alkaloid nor a glucoside, made no attempt to characterise it (*Arb. pharm. Inst. Dorp.*, 1892, **8**, 5). Shortly afterwards, E. Merck (*Merck's Ann. Report*, 1895, 123) pointed out that if the observation, made by Henkel and by Engelhardt, that hyenanchin exerts a strychnine-like action on the brain, but is without action on the spinal cord, is trustworthy, the substance might be of some therapeutic value as a substitute for strychnine in cases where cerebral action alone is required.

For a supply of the plant, the author is indebted to Mr. I. B. Pole Evans, Chief of the Division of Botany, Department of Agriculture, Pretoria.

Experimental.

The material used included stems (1 kilo.), leaves (2 kilos.), and fruits (4 kilos.). Each of these parts of the plant was extracted separately with chloroform in a continuous, hot percolation apparatus, yielding, in the case of the stem and leaves, a hard, dark green wax, and in that of the fruits a neutral, dark yellow oil, which was not examined in detail. Extraction was continued with hot 95 per cent. alcohol, and the liquid concentrated to a thin syrup, which was poured into five volumes of water, causing the separation of sparingly soluble tannin containing a small amount of a yellow colouring matter. The filtrate, after purification with lead acetate in the usual manner, was concentrated under reduced pressure to a viscid syrup, which was then extracted repeatedly with an equal volume of ethyl acetate until it was free from bitterness and no longer toxic. The brown, sticky residue left on distilling off the ethyl acetate was dissolved in three times

its weight of water and set aside, when, after some weeks, a bitter, poisonous, crystalline material separated. Mere traces of this were obtained from the leaves and stems, and only 6 grams from the fruits (0·15 per cent.), but this does not represent all that is present, as the mother liquor was still toxic and intensely bitter, and in the case of the fruits a further 1·7 grams (making a total yield of 0·19 per cent.) were obtained by repeating the treatment with ethyl acetate.

This crude material could only be recrystallised by adding it to fifty times its weight of boiling water and filtering rapidly, when, on cooling, there separated a crop of slender, colourless needles. Slight concentration of the filtrate gave a further crop of the same substance, and reduction of the mother liquor from this crop to half its original volume led to the separation of a second substance, crystallising in short, colourless, hexagonal prisms, of which more was obtained by further concentration. This second substance forms about two-thirds of the original crystalline material, and it is proposed to apply to it Engelhardt's name, hyenanchin; as the substance crystallising in needles is an isomeride of this, it may appropriately be called iso*hyenanchin*.

Hyenanchin.

This substance, isolated as described above, and purified by repeated recrystallisation from boiling water, has no melting point, but when heated becomes yellow at 200°, then darkens, and finally decomposes sharply, with effervescence, at 234°. It dissolves in water to the extent of 1·18 per cent. at 15°, is more soluble in boiling water, and sparingly so in alcohol, butyl alcohol, ethyl acetate, or acetone. It has $[\alpha]_D^{15} + 14·7°$ in water (Found: C = 58·2, 58·3, 58·05, 57·9; H = 6·03, 6·01, 6·4, 6·3. Loss at 110° in a vacuum, nil. $C_{15}H_{18}O_7$ requires C = 58·06; H = 5·8 per cent.).

Hyenanchin contains no nitrogen, reduces Fehling's solution on boiling, and silver nitrate solution on gently warming or on keeping in the cold, decolorises permanganate immediately, and gives an amorphous, yellow precipitate with bromine water. Boiling dilute hydrochloric acid converts it into an amorphous, brown substance, which gives a characteristic, orange-coloured, amorphous precipitate with phenylhydrazine in the cold. No sugar is produced. On warming with alkalis, hyenanchin furnishes a distillate containing a minute quantity of a substance, which gives the iodoform reaction, reduces Fehling's solution, and furnishes a semicarbazone, crystallising in short, colourless needles, and decomposing at 200°, which may be acetolsemicarbazone, $C_4H_9O_2N_3$ (decomp. 195—200°) (Found: N = 31·12. Calc.: N = 32·06 per

cent.). A specimen of acetolsemicarbazone, prepared under similar conditions, and without recrystallisation, gave N = 30·8 per cent., and a mixture of the two decomposed at 198°. No derivatives of hyenanchin with hydroxylamine, phenylhydrazine, or semicarbazide could be obtained.

Action of Baryta.—Although hyenanchin is not acid to indicators, it neutralises alkalis, but its titration presents difficulty, owing to the ease with which it becomes coloured and decomposes in presence of alkalis. If a solution of hyenanchin to which excess of baryta has been added is warmed or kept for several days, it becomes brown and turbid, the latter due to the gradual separation of barium carbonate. By dissolving it in *N*/5-baryta and at once titrating with *N*/5-sulphuric acid in the presence of phenolphthalein, a fairly satisfactory end-point is obtained (Found: $Ba(OH)_2$ required for neutralisation, 55·2, 55·05. Calc. for two CO_2H groups, 55·3 per cent.).

On evaporating in a vacuum the filtrate from the barium sulphate formed, barium carbonate is gradually deposited, and the filtrate from this yields, on complete evaporation in a vacuum, a nearly colourless varnish, which appears to consist chiefly of a barium salt of a monocarboxylic acid, since it yields on addition of excess of *N*/5-sulphuric acid 29·8 per cent. of its weight of barium sulphate ($C_{28}H_{42}O_{14}Ba$ requires $BaSO_4 = 31·5$ per cent.). The corresponding *acid*, obtained by adding the calculated quantity of *N*/5-sulphuric acid to an aqueous solution of this salt and evaporating the filtrate to dryness in a vacuum, is a colourless varnish, which is readily soluble in water, and reduces Fehling's solution on boiling and ammoniacal silver nitrate in the cold. The acid does not regenerate hyenanchin on drying, even at 150° in a vacuum.

These results indicate that hyenanchin is probably a dilactone, convertible by the carefully regulated action of weak alkali into the corresponding dihydroxydicarboxylic acid, $C_{15}H_{22}O_9$, which is unstable and readily loses one carboxyl group.

Action of Acetic Anhydride.—When hyenanchin is heated with acetic anhydride at 100°, most of it crystallises out unchanged on cooling, but if a drop of pyridine be added and the heating continued, it is converted into a soft, sticky resin, from which with great difficulty there can be separated, by repeated crystallisation from dilute alcohol, a small yield of crystalline material consisting of at least three substances: (*a*) cream-coloured needles, softening at 136° and finally melting and decomposing at 169°; (*b*) colourless needles, m. p. 126°; (*c*) colourless, short needles, m. p. 104°. Only a few centigrams of each of these substances were obtained,

so that they could not be satisfactorily purified for examination, but it is probable that only the second is a true acetyl derivative of hyenanchin (Found: C=56·7, 57·05; H=5·7. $C_{15}H_{17}O_7Ac$ and $C_{15}H_{16}O_7Ac_2$ require C=57·9; H=5·6 per cent.).

iso*Hyenanchin*.

iso*Hyenanchin* crystallises from boiling water in long, slender needles with a silky lustre, has no melting point, but becomes brown at 245° and decomposes sharply, with effervescence, at 299°. It dissolves in water to the extent of 0·26 per cent. at 15°, is somewhat more soluble in boiling water, and less so in alcohol or ethyl acetate. $[\alpha]_D^{15}$ −61·3° in water (Found: C=58·08, 58·25; H=5·97, 6·16. $C_{15}H_{18}O_7$ requires C=58·06; H=5·80 per cent.). It reduces Fehling's solution on boiling and ammoniacal silver nitrate in the cold.

Action of Baryta.—*iso*Hyenanchin dissolves immediately in excess of *N*/5-baryta solution, forming a solution, which only becomes slightly yellow after remaining several days at 0°, and under these conditions combines with sufficient baryta to neutralise one carboxyl group (Found, on immediate titration, 29·8; after three days at 0°, 29·2. Calc. for one CO_2H group, 27·7 per cent.). On again adding excess of *N*/5-baryta solution and boiling gently for a few minutes and titrating back, baryta equivalent to a second carboxyl group is found to have been absorbed (Found: 25·9. Calc.: 27·7 per cent. Total for two CO_2H groups=55·4. Calc.: 55·3 per cent.). A second estimation, made by heating *iso*hyenanchin with excess of *N*/5-baryta solution for one hour at 100° and titrating back, gave 56·2 per cent. The filtrate from these estimations, on concentration, behaved like the similar preparation from hyenanchin (p. 1621), and gave as a final residue an amorphous barium salt, yielding 29·1 per cent. of barium sulphate on precipitation with *N*/5-sulphuric acid.

Physiological Action of Hyenanchin and iso*Hyenanchin.*

The author is greatly indebted to Dr. J. Trevan, of the Wellcome Physiological Research Laboratories, who kindly undertook the examination of a series of preparations of *Hyenanche*, and finally of the pure substances isolated. Dr. Trevan reports that hyenanchin has a physiological action almost identical in kind with that of picrotoxin, but is much weaker. *iso*Hyenanchin, on the contrary, is not toxic in such doses as can be injected intravenously.

Relationship of Hyenanchin and iso*Hyenanchin to other Non-nitrogenous Convulsant Poisons.*

The reactions described above and the physiological action of hyenanchin indicate that the latter belongs to the group of convulsant, non-nitrogenous poisons, of which picrotoxinin, $C_{15}H_{16}O_6$ (m. p. 206·5°, $[\alpha]_D$ +4°40′ in alcohol), coryamirtin, $C_{15}H_{18}O_5$ (m. p. 225°, dextrorotatory), and tutin, $C_{17}H_{20}O_7$ (m. p. 208—209°, $[\alpha]_D$ +9·25° in alcohol), are the only well-defined members known. Associated with picrotoxinin in the molecular compound, picrotoxin, $C_{30}H_{34}O_{13}$, is the substance, picrotin, $C_{15}H_{18}O_7$ (m. p. 245—246°, $[\alpha]_D$ −55·2° in water), which is not toxic. Picrotoxinin and picrotin are both dilactones, and are now believed to contain, respectively, one and two hydroxyl groups, the function of the sixth and seventh oxygen atoms, respectively, being still unknown (Horrmann, *Annalen*, 1916, **411**, 273). Both these substances yield small quantities of acetone on distillation with alkali. Picrotin is isomeric with hyenanchin and *iso*hyenanchin, and in many ways is very similar to the latter. The two have therefore been carefully compared, and found not to be identical, the chief differences being that picrotin has a definite melting point and is completely converted into the corresponding dicarboxylic acid by baryta in the cold, whilst *iso*hyenanchin has no definite melting point, and is converted into the corresponding dicarboxylic acid by baryta in two well-defined stages. A mixture of both substances begins to sinter at 225°, which is well below the melting and decomposing points of the two components. A number of substances of the formula $C_{15}H_{18}O_7$ have also been prepared from picrotoxinin and picrotin (compare Horrmann, *loc. cit.*), namely, picrotin–lactone (338°, decomp.), picrotoxic acid (m. p. 230—231°, $[\alpha]_D$ +81·7°, crystallises with $2H_2O$), α-picrotoxinic acid (m. p. 209°, $[\alpha]_D$ −48°), and β-picrotoxinic acid (m. p. 235°, $[\alpha]_D$ −48°). None of these closely resembles either hyenanchin or *iso*hyenanchin.

Subsidiary Constituents of Hyenanche globosa.

Examination of the Wax. Isolation of a New Phytosterol and a New Wax Alcohol.

The dark green wax from the leaves and stems was mixed with an equal weight of animal charcoal, and extracted with boiling ethyl acetate, yielding a greenish-yellow solution. This, on cooling, deposited a mixture of two substances, which were separated by heating the solution to boiling and adding enough ethyl acetate

to keep both substances dissolved at 35°. On keeping, the liquid then deposited gelatinous granules, which filtered with difficulty, and, on drying in the air, formed a pale brownish-green, horny mass. This was purified by distillation in a vacuum and recrystallisation from ethyl acetate, when it formed colourless masses of minute needles melting at 82—83° (corr.). A number of solid alcohols melting near this temperature are known, but all of them differ slightly in composition and most of them in crystalline form from hyenanche alcohol, and of those tried, ceryl, myricyl, and wheat* alcohols, all depressed the melting point. It is readily soluble in chloroform, boiling ethyl acetate, or alcohol, and sparingly so in ether, does not combine with bromine, and appears to be a new saturated *alcohol* of the formula $C_{24}H_{49}\cdot OH$ (Found, in substance dried at 60° in a vacuum: C = 81·02, 81·27, 81·19†; H = 13·5, 13·55, 13·89.† $C_{24}H_{50}O$ requires C = 81·3; H = 14·1 per cent.).

When boiled for several hours with acetic anhydride in presence of pyridine, it yields an *acetyl* derivative, which is readily hydrolysed on recrystallisation from most solvents, but separates from acetic anhydride in soft masses of colourless needles melting at 75° (corr.) (Found: C = 78·8; H = 13·0. $C_{26}H_{52}O_2$ requires C = 78·7; H = 13·1 per cent.).

Carnaubyl alcohol, which also has this formula, crystallises in leaflets (m. p. 68—69°), and is quite distinct from the alcohol of *H. globosa*. The other known alcohols of this formula are either liquid or of much lower melting point than *Hyenanche* alcohol.

The filtrate from the alcohol on concentration deposited a second substance, which, after repeated crystallisation from boiling ethyl acetate, forms long, lustrous needles melting at 265° (corr.), is readily soluble in chloroform or boiling ethyl acetate, and sparingly so in alcohol, even on boiling (Found: C = 83·66, 83·95; H = 11·35, 11·66. $C_{28}H_{46}O$ requires C = 84·4; H = 11·55 per cent.). $[\alpha]_D^{15}$ −22·4° in chloroform.

It gives a typical phytosterol reaction with sulphuric acid in the presence of acetic anhydride, and furnishes a *monoacetyl* derivative, crystallising from hot ethyl acetate in small, spheroidal masses of colourless needles melting at 244° (corr.) (Found: C = 81·12; H = 10·96. $C_{30}H_{48}O_2$ requires C = 81·8; H = 10·9 per cent.).

This substance appears to be a new phytosterol belonging to the series represented by the general formula $C_nH_{2n-10}O$, of which at least eight are now known, beginning with alcornol, $C_{22}H_{34}O$

* For a specimen of this alcohol the author is indebted to Mrs. M. T. Ellis (*Biochem. J.*, 1918, **12**, 160). † Regenerated from acetyl derivative.

(Hartwich and Dünnenberger, *Arch. Pharm.*, 1900, **238**, 348), and terminating with amyrin, $C_{30}H_{50}O$ (Windaus and Welsch, *ibid.*, 1908, **246**, 506). The new phytosterol is exceptional in this series in being lævorotatory and in giving an acetyl derivative melting at a lower temperature than the parent substance, but in all other respects it resembles other members of the series.

Isolation of a New Yellow Colouring Matter.

The colouring matter was obtained in small amount (total, 2·3 grams crude, 1·0 gram pure, from all three sources) by extracting the sparingly soluble tannin (p. 1619) with boiling dry ether, and was recrystallised from alcohol, from which it separated on slow evaporation in microscopic, yellow needles, which became brown at 200°, and finally melted and decomposed at 270—280°. It is moderately soluble in alcohol, sparingly so in ether, and insoluble in chloroform. The solution in alcohol gives a brownish-black precipitate with ferric chloride (Found: C=62·43, 62·1,* 62·1*; H=4·4, 4·4,* 4·25.* Loss in a vacuum at 100°, 10·08. $C_{15}H_{12}O_6$ requires C=62·5; H=4·16. $C_{15}H_{12}O_6,2H_2O$ requires loss 11·1 per cent.).

The colouring matter furnished an *acetyl* derivative, crystallising from hot alcohol in masses of cream-coloured needles melting at 234—236° (decomp.; corr.) (Found: C=63·4; H=4·0. Loss at 60° in a vacuum, nil). On regeneration with hydrochloric acid in the presence of hot acetic acid, the acetyl derivative yielded 71·3 per cent. of colouring matter identical with the original substance. Sulphuric acid could not be used for this purpose, as it appeared to convert the colouring matter into a soluble sulphonic acid (compare A. G. Perkin, T., 1899, **75**, 448). These results indicate that the acetyl derivative should be represented by the formula $C_{15}H_7O_5Ac_3$ (requires C=63·6; H=4·04; colouring matter, 72·7 per cent.), which is a triacetyl derivative of the parent substance, less one molecule of water. The reactions of the colouring matter indicate that it belongs to the flavone group, in which the loss of a molecule of water on acetylation does not appear to have been recorded previously, except doubtfully in the case of morin (A. G. Perkin, *loc. cit.*). Unfortunately, the small amount of material available precluded further investigation of this and other points.

WELLCOME CHEMICAL RESEARCH LABORATORIES.

[*Received, November 26th*, 1920.]

* Regenerated from acetyl derivative.

OBITUARY NOTICES.

AUGUSTUS GEORGE VERNON HARCOURT.*

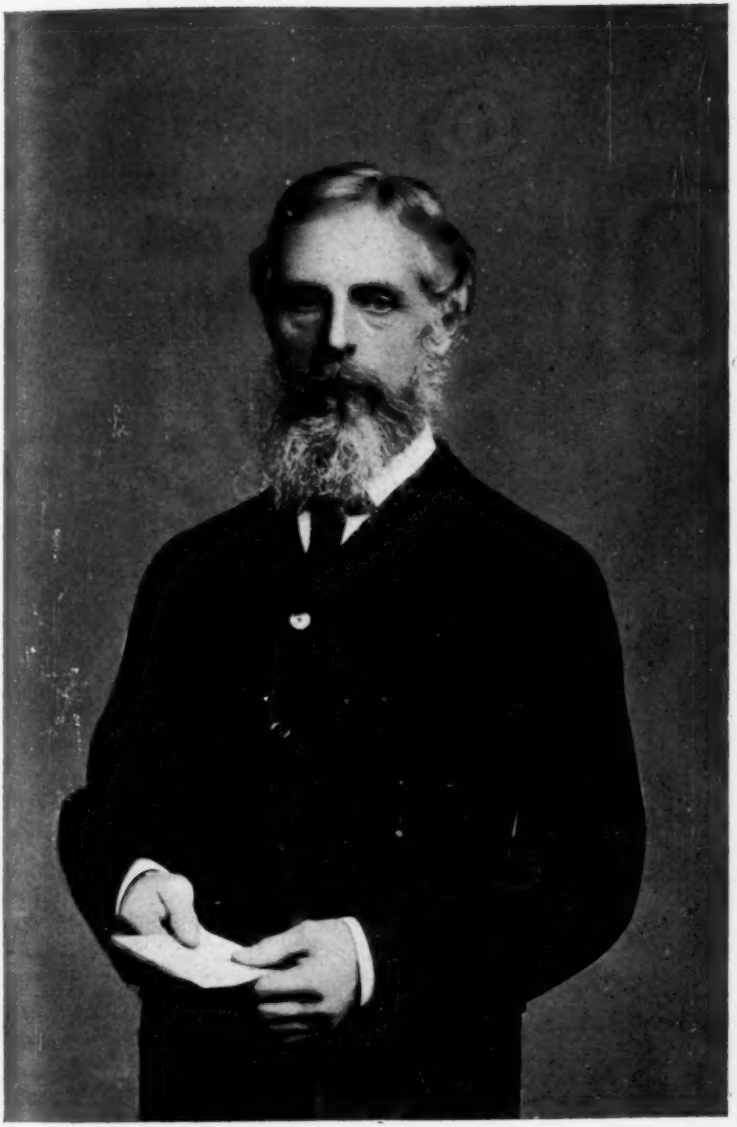
BORN DECEMBER 24TH, 1834; DIED AUGUST 23RD, 1919.

BY the death of A. G. Vernon Harcourt in his eighty-fifth year, there passed away a chemical teacher endeared to many generations of Oxford students, a singularly skilful experimenter, and a pioneer in the new domain of physical chemistry. He was one of the first who planned experiments to follow the course of a chemical change, to measure the velocity of a reaction, and to study the conditions that determine it; he rebelled against the idea that chemists had to concern themselves only with the preparation of new substances and the elucidation of their properties—for him the interesting thing was *how* the change happened, not what was the result.

Augustus George Vernon Harcourt was the elder son of Admiral F. E. Vernon Harcourt and of Marcia, sister of the first Lord Tollemache, and grandson of the Archbishop of York. He was born December 24th, 1834, and died August 23rd, 1919. He was educated on the old classical lines at Cheam and at Harrow, and entered Balliol College, Oxford, in 1854.

It was at Balliol, under Henry Smith, that he laid the foundation of his chemical career. Harcourt, in his reminiscences of the Oxford Museum and its Founders, has told us how, when Salvin's buildings at Balliol were constructed early in the "fifties," two cellars were appropriated to the study of chemistry; and to provide a teacher, Henry Smith, ablest of Oxford men, was deputed by the College to take some lessons in the subject. He went for a few months to Dr. Hofmann at the College of Chemistry. Montgomerie, Hertford Scholar in 1854, and Harcourt were his first pupils. The classical atmosphere of the College cellar is brought out in one of Harcourt's reminiscences: "Once a stick of phosphorus took fire on the bench; Montgomerie was for pouring water over it, which might have caused a dangerous scattering of the fiercely burning liquid; Henry Smith stopped him, and extinguished the blaze by pouring over it a little sand, remarking in his soft tones—'*Pulveris exigui jactu compressa quiescet.*'"

* Reprinted by permission from the *Proceedings of the Royal Society*.



A. V. Harcourt.

[*To face p.* 1626 *Trans.*

When Brodie, a pupil of Bunsen, came to Oxford as Professor of Chemistry, the Balliol cellars were placed at his disposal, and Harcourt became first his pupil and then his assistant. At Balliol, Brodie began working on the acid peroxides, and afterwards on the oxidation of graphite, and then turned to the systematic study of the alkaline peroxides, the reducing action of which he was the first to explain—incidentally supplying a strong *chemical* argument in favour of the diatomic nature of oxygen gas. In 1858, Brodie migrated to the chemical department of the New Museum, and took Harcourt—still an undergraduate—with him as lecture assistant. A year later, after gaining a First Class in the School of Natural Science, Harcourt was appointed Demonstrator in the Students' laboratory, known from its prototype as the "Glastonbury Kitchen"—and among his first pupils was the Prince of Wales, afterwards King Edward VII.

Under Brodie, at the New Museum, Harcourt began his researches with the exact determination of the oxygen absorbed by the metals potassium and sodium—allowing air to enter slowly into a flask containing the pure liquid metal heated in an atmosphere of nitrogen. In this first paper one can see that it is the initiation and progress of the oxidation that interest him. "Soon after the dry air has begun to mix with the nitrogen, the grey film which covers the molten metal changes to a deep blue; the surface gradually becomes roughened by little wrinkles and projections, and a moment arrives when a single spluttering spark appears at one point and a dust of white oxide rises. . . . At the point where the spark appears the blue crust becomes white, and this change passes in a moment over its whole extent."

In 1859 Harcourt was elected Lee's reader in chemistry and a senior student of Christ Church, but it was not until some years after his appointment that he began his work in the Lee's Laboratory. Meanwhile he had started those researches on the rate of chemical change which—in conjunction with those of Berthelot in France and those of Guldberg in Norway—were to establish on a quantitative basis Berthollet's law of mass action. In the interpretation of his results Harcourt was associated with William Esson, whose special mission in Oxford seemed to be—as the writer knew him—to illuminate mathematically the obscure records of chemical velocities. Harcourt and Esson first studied the reaction between oxalic acid and potassium permanganate in acid solution. They found that the rate of change varied with the amount of manganous sulphate formed, and that the reaction was probably *nil* in the complete absence of manganous salt; but, once started, the velocity would increase to a maximum and then fall off—the

curve representing the course of the change having a point of contrary flexure. They liken their curves to those obtained by Bunsen and Roscoe in the course of photochemical induction—thus suggesting that the "inductive period" in the union of hydrogen and chlorine was due to the action of another substance, a suggestion which finally was proved to be correct.

Seeking for a less complicated reaction, Harcourt found that in dilute solutions hydrogen peroxide decomposed hydrogen iodide with velocities that could be easily followed, and the amount of change could be accurately ascertained. The method of carrying out the experiment in a stream of carbon dioxide, and the device by which the iodine liberated was reconverted into iodide by the successive additions of exactly equal drops of concentrated thiosulphate, show Harcourt at his best as an experimenter. The time-intervals between the successive appearances of the iodine proved that the velocity of the change varied directly with the quantities of each of the reacting substances—when the other conditions were kept constant. The rates found, however, do not prove that the change is necessarily a termolecular one as Harcourt supposed:

$$H_2O_2 + 2HI = 2H_2O + I_2.$$

The change most probably takes place in two stages, each of which is bimolecular; but, one stage being much faster than the other, the observed rates follow the simple law. In studying the effect of temperature on the rate of this reaction, Harcourt and Esson arrived at a zero of chemical action in wonderful agreement with the absolute zero calculated from physical data.

Harcourt was so strongly convinced that chemical change followed mechanical laws that his laboratory became a centre where the experiments of Bunsen and his school on "chemical induction" and "sprungweise" explosions were repeated and criticised.

Though one of the pioneers of physical chemistry, Harcourt remained a sceptic towards the new theories of solution and ionisation, and the word "dissociation" was anathema to him. In his last address as President of the Chemical Society in 1897, he maintained that the distinction between dissociation and decomposition was absurd. "A journey," he declared, "is the same journey, whether I go with a return ticket or whether I cannot return by the same route."

Of the painstaking character of Harcourt's demonstrations, of his insistence on neatness and cleanliness, of the patience and personal trouble he took with each beginner, generations of old Christ Church men can speak with grateful appreciation. The

minutiæ of manipulation appealed to him, but they were only means to attack the largest problems; for him no defect was too small to remedy, no authority was too great to question. Through the inspiration of his example and teaching, Oxford, no less than English chemistry, has been intellectually quickened.

In applied chemistry Harcourt was chiefly drawn to questions dealing with the purification and testing of coal-gas, he having been appointed in 1872 one of the three Metropolitan Gas Referees whose duty it is to prescribe the mode of testing the London gas and, subject to the various Acts of Parliament, to fix the limits of impurity allowed. One of his early researches on coal-gas was his attempt to purify the gas from sulphur compounds by means which he devised for converting the carbon disulphide into hydrogen sulphide. Harcourt's "sulphur test" came into wide use, but its application on a large scale for the purification of coal-gas has only recently been carried out successfully by Dr. Charles Carpenter at the South Metropolitan Gas Works. Perhaps the most signal improvement in the testing of gas effected by Harcourt was the introduction of the Pentane Lamp as the official standard of light in place of the variable spermaceti candle. His original one-candle lamp has been replaced by the more convenient 10-candle Pentane lamp, and this has been largely adopted as the measure of illuminating power, not only for gas, but for other illuminants.

Another very useful investigation which occupied much of his time between 1899 and 1911 was concerned with the administration of chloroform as an anæsthetic. Already in the former year he had devised a ready means for determining the percentage of chloroform vapour, mixed with air, by converting the chloroform into carbon dioxide and hydrogen chloride in contact with a red-hot platinum wire in presence of steam and of water to absorb the hydrogen chloride:

$$2CHCl_3 + 2H_2O + O_2 = 2CO_2 + 6HCl.$$

When the Council of the British Medical Association in 1901 appointed an expert committee to investigate the methods in use for administering chloroform, to study its quantitative determination, and "to determine if possible what is the minimum dose which would secure anæsthesia for operations and at the same time not endanger life," they gave their committee power to co-opt two outside members—of whom Harcourt was their first choice.

After much patient labour he devised an "inhaler," which his colleagues described as "possessing the advantages of simplicity, exactness, and portability." The Committee adopted it in their experiments, and in their final Report state that it appears to be well adapted for universal employment.

Of recognition by learned societies and of devoted service rendered to them Harcourt could claim a large share. Elected to the Royal Society in 1863, he served on the Council 1878—80. In conjunction with Esson, he published four memoirs in the *Philosophical Transactions*, in the third of which, the Bakerian Lecture for 1895, the observations are given indicating that all chemical action would cease at $-272{\cdot}6°$.

Admitted to the Chemical Society in 1859, he served as one of its Secretaries for eight years, 1865—73, and was elected President in 1895. In 1910 he was one of the five Past-Presidents whose jubilee as Fellows was celebrated by the Society.

As became the nephew of one of the founders of the British Association—Rev. W. Vernon Harcourt—he early took an interest in its meetings and made many contributions to the Chemical Section, of which he was President in 1875. A few years later he was elected one of the General Secretaries of the Association, an office he held for fourteen years with conspicuous tact. He was an honorary Doctor of Oxford, McGill, and Durham Universities.

In 1872 Harcourt married Rachel Mary, daughter of Mr. H. A. Bruce, at that time Home Secretary in Mr. Gladstone's first administration, and afterwards Lord Aberdare. Of his happy family life at Cowley Grange, the home he built for himself on the banks of the Cherwell, many of his old Oxford pupils and friends can tell; and perhaps no more picturesque spot could have been chosen for the evening of his days than St. Clare, near Ryde, the property he inherited, with its fine cedars and beautiful lawns falling from terrace to terrace down to the waters of Spithead. Even in the sunny Isle of Wight people spoke of the roses of St. Clare—that pleasantest corner of the world of which he would quote when bidding one to an Easter or an autumn visit:

> "*Ver ubi longum tepidasque praebet*
> *Juppiter brumas.*"

Both at Oxford and St. Clare, Harcourt displayed extraordinary activity in games. Without being an athlete, he was naturally fond of all sports and outdoor exercises, and, once interested in a game, he took infinite trouble to improve. Many of his pupils found, to their surprise, that their white-haired tutor could give them lessons in other things besides chemistry.

His knowledge of the classics, especially of poetry, and a memory which remained excellent till quite late in life, made him apt at quotation and ready in rejoinder. He was a really good critic of style. Singularly lucid as a writer, he set his pupils an example

of precision and clearness, which some, it must be admitted sorrowfully, could not reach, though they tried to follow it.

His life was a full and happy one; he followed the path he had chosen, with never a thought for profit or self-advancement. If he had an ambition, it was the desire to serve others, and to feel that he was loved by his friends.

Few men have been so completely happy in their work or lived so much in the lives of their students. The writer, whose good fortune it was to fall under his influence at Oxford, gratefully acknowledges that he owes his career to Harcourt's affectionate interest and to his example. H. B. D.

LUCIUS TRANT O'SHEA.

BORN MARCH 29TH, 1858; DIED APRIL 18TH, 1920.

LUCIUS TRANT O'SHEA, the eldest son of Major R. P. O'Shea, was born in 1858. He was proud of being the grandson of Sir Lucius Curtis, admiral, and still more proud that he was descended from the distinguished admiral Lord Rodney.

He was educated at the Manchester Grammar School, and completed his chemical training under Roscoe at Owens College. Afterwards he acted as private assistant to C. Schorlemmer, and took part in the research on the constitution of aurine.

Later he was chemist in an explosives factory, where he gained experience which was valuable to him in after-life.

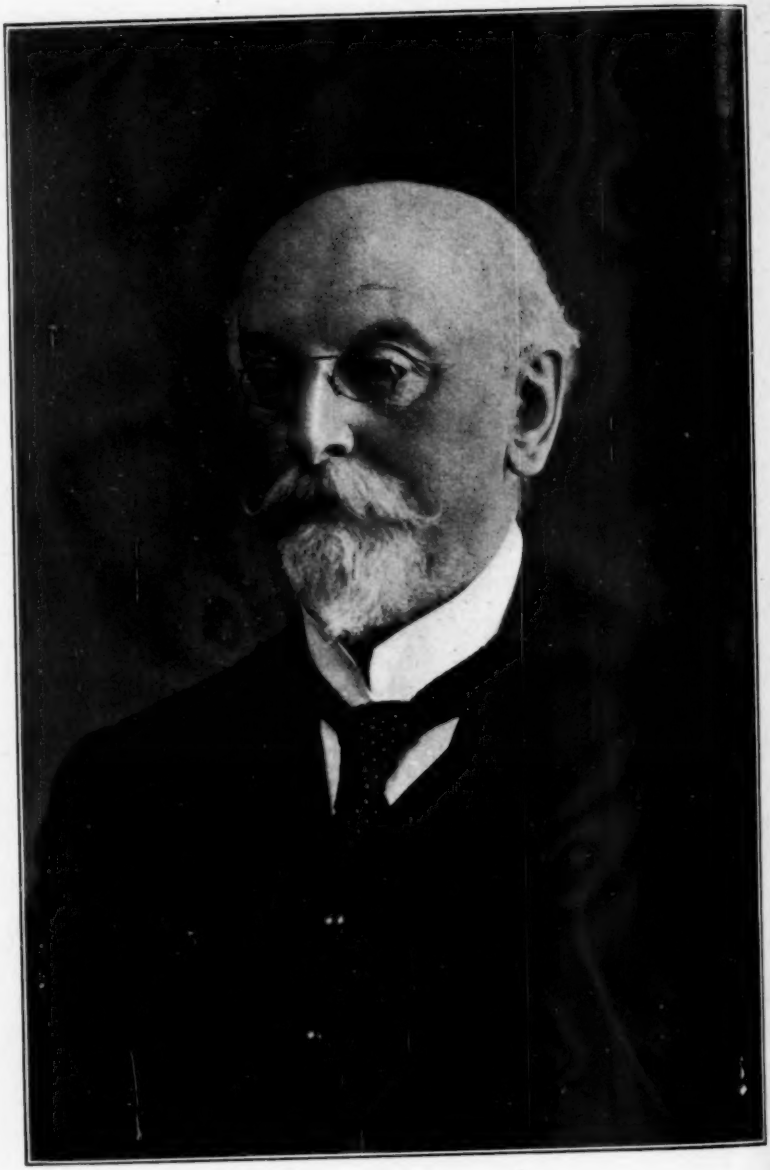
When Firth College, Sheffield, was opened, Thomas Carnelley was appointed Professor of Chemistry and Physics. He selected O'Shea as his assistant lecturer and demonstrator in chemistry in 1881. Later O'Shea held the post of lecturer in mining chemistry, and in 1907 he was appointed Professor of Applied Chemistry in the University of Sheffield. He remained faithful to the college and its allied institutions to the day of his death, which took place suddenly on April 18th, 1920, a period of thirty-nine years.

O'Shea was a B.Sc. of London and an M.Sc. of Sheffield. For a time he was an abstractor for this *Journal*. His genial nature and courteous demeanour won the regard and esteem of all who knew him. Children adored him, and the success of a children's party was ensured by his presence.

For several years his energies were devoted to imparting a

knowledge of chemistry and physics to the deputies (*in futuro*) in the coal-mining districts of Derbyshire and the neighbourhood of Sheffield. This was probably his most valuable work in the early days of Sheffield University College. The results of this teaching are embodied in an exceedingly useful book, "Elementary Chemistry for Coal Mining Students," published in 1911, which was specially intended for students who had little or no preliminary knowledge of chemistry. O'Shea's most important contributions to pure chemistry are papers on the "Constitution of Bleaching Powder" and on the "Preparation of Pure Iron," which are to be found in the pages of this *Journal* and in the *Journal* of the Society of Chemical Industry. He also made a number of contributions on the applications of Chemistry to mining problems, especially in connexion with explosions in coal mines, mining explosives, the by-products of coking, coal-washing, etc. These are to be found for the most part in the *Transactions* of the Institution of Mining Engineers.

His work in connexion with mining brought him into intimate contact with a large number of prominent mining engineers, by whom his admirable qualities were fully appreciated. In 1905 he was elected Secretary of the Midland Institute of Mining, Civil, and Mechanical Engineers. In 1908 the Institution of Mining Engineers, which had for many years had its headquarters at Newcastle-on-Tyne, decided to move these to London; simultaneously, the Institution was in many respects reorganised, and, the general secretary having died in the previous year, it was decided after much deliberation to offer the honorary secretaryship to Professor O'Shea, which the latter accepted, and he was duly appointed to the post on September 2nd, 1908, with an assistant secretary in London to attend to the routine work. It must be understood that this honorary secretaryship was anything but a sinecure, as the reorganisation of a complex society like the Institution of Mining Engineers demanded much hard work and involved a mass of correspondence; what was, however, needed more than anything to ensure the success of the altered conditions was the power to reconcile various conflicting interests, and in this the tact, geniality and shrewdness of O'Shea proved invaluable. He continued to hold the post of honorary secretary until the time of his death, and discharged all the duties of that post in a thoroughly admirable manner; during his tenure of the office he did much to strengthen and consolidate the Institution of Mining Engineers and to maintain the *Transactions*, for the editorship of which he was responsible, at the highest possible standard.



[*To face p.* 1633 *Trans.*

O'Shea was a keen volunteer, and took an active part in raising a company of the 1st West York R.E. Volunteers. In the Boer War he went out to South Africa in command of a detachment of this company. This experience of active service led to his being placed in command of the University O.T.C. contingent, which was formed in 1911, a position he retained for eight years.

Valuable service to the country in training officers was accomplished during the Great War.

O'Shea leaves a widow and one daughter.

W. C. W. AND H. L.

JAMES EMERSON REYNOLDS.*

BORN JANUARY 8TH, 1844; DIED FEBRUARY 17TH, 1920.

JAMES EMERSON REYNOLDS was born at Booterstown, Co. Dublin, on January 8th, 1844. He was the son of Dr. James Reynolds, a medical practitioner at Booterstown, a man of some literary ability and the author of one or two plays which had a certain measure of success. His mother, originally a Miss Campbell, was English. He was named after his great uncle, a Captain Emerson, of the Royal Navy.

Emerson Reynolds, as he was usually called, was intended for the medical profession, and in early youth became an assistant to his father. In 1865 he qualified as a licentiate of the Edinburgh College of Physicians and Surgeons, and afterwards practised for a short time in Dublin; but on his father's death he definitely abandoned medicine, and, following a strong inclination, devoted himself solely to chemistry. At Booterstown he had fitted up a small laboratory, and tried his hand at research work from the outset.

He was not a student of Trinity College, and never attended a systematic course of instruction either in theoretical or practical chemistry. In fact, he was wholly self-taught. His first paper, "On the Oleaginous Matter formed on dissolving different kinds of Iron in Dilute Acids," appeared in the *Chemical News* for 1861, when its author was, presumably, only seventeen years of age. In the same year, and in the same volume, appeared a second paper, "On a New Process for Photographic Printing." These were followed, next year, by a communication to the same journal on

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the "Oxalates of Iron," and in 1863 by no fewer than five contributions, partly to the *Chemical News* and partly to the *Journal* of the Royal Dublin Society. Their various subjects—"On the Economical Preparation of Sulphocyanide of Ammonium" (*Chem. News*, 1863, **8**, 14), "On the Numerical Nomenclature of Spectral Lines" (*idem*, p. 59), "On the Detection of Hyposulphite of Soda" (*idem*, p. 283), "Wood Spirit and its Detection" (*J. Roy. Dubl. Soc.*, 1863, **4**, 126), "Note on Pure Methylic Alcohol" (*idem*, p. 131)—if of no special merit or great originality, are, at least, remarkable as the work of a self-taught youth, wholly unguided, and with very limited means. They serve to show the range of his activities and the assiduity with which he followed the developments of contemporary science. Spectrum analysis was only in its infancy in 1863. Reynolds' practical interest in the subject was probably quickened by the popular lectures of the late Sir Henry Roscoe and Sir William Huggins to the Royal Dublin Society, and, as subsequent papers show, he maintained this interest to the end of his days. His early work was carried on under considerable difficulties, and as it was probably regarded as an interruption to his medical studies, it is doubtful if it received much encouragement at home. It was not until 1867, when he became keeper of minerals at the National Museum in Dublin, that he had access to a fairly equipped chemical laboratory. The subject-matter of many of his papers from 1868 onwards—for example, formation of dendrites, manganese ores, phosphoric acid in minerals, classification of silicates, notes on Irish rutile and the felspars, boron minerals, mineralogical tables, etc., etc.—may be said to have had their origin in this appointment; and it was probably due to the interest thus created in the chemistry of silicon, which he laboured to show was conceivably co-extensive with that of carbon, that we owe his many papers on the silicic acids, silicon haloids, and on silico-organic compounds, which he continued to publish, from time to time, down to his last paper in 1913.

To this early work belongs his discovery of the colloidal derivative of mercury and acetone (*Proc. Roy. Soc.*, 1871, **19**, 431), which originated from his experiments on wood-spirit. It was the first colloidal derivative of mercury to be made known. The neutral solution of the compound $(C_3H_6O_2),3HgO$, prepared by dialysis, was used with success by the late Sir Charles Ball as an antiseptic dressing in surgery where no ordinary mercurial solution could be used.

In 1868 he became analyst to the Royal Dublin Society, and two years later was appointed Professor of Chemistry at the Royal College of Surgeons, Dublin. He held both these positions until

his election, in 1875, to the Chair of Chemistry at Trinity College, Dublin, as successor to Dr. James Apjohn. At this period Reynolds had a considerable practice as a consultant and public analyst. He was interested in subjects relating to medical chemistry and hygiene, and had collaborated in the production of a "Manual of Public Health for Ireland." He was responsible for the analytical examination of the Vartry water as supplied to Dublin, and had laboured, like many before and since, at the perennial question of the utilisation of Irish peat.

On his appointment to Trinity College, Reynolds devoted himself, almost exclusively, to the duties of his chair. He was a good lecturer and an excellent teacher, somewhat precise in manner and diction, and too strict a disciplinarian to be generally popular with the type of student he had to teach; but he always commanded the respect of his pupils, who could appreciate the care and thought he spent on his lectures. They were always admirably illustrated by experiments, for he spared no pains in acquiring or devising suitable and striking demonstrations. If an experiment failed, which rarely happened, he insisted on its successful repetition on the next occasion. He was scrupulously careful that his teaching should be abreast of contemporary knowledge. He early perceived the significance and value of the doctrine of Periodicity, and his course of instruction was arranged in conformity with it. His theoretical conceptions of the basic principle of the Law, afterwards expanded by Sir William Crookes, and his graphic and glyptic representations of it, are well known to teachers of chemistry. He was among the first to attempt to settle the true position of the element glucinum in the periodic series, and to establish its valency and atomic weight. It is true that the experimental proof he was able to adduce was not wholly convincing, as the metal which he had himself prepared was far from pure, and the foreign matter present necessitated a very uncertain correction. It was only subsequently established that the specific heat of glucinum, as in the case of other elements of low atomic weight, varied very rapidly with the temperature, and that it was only at comparatively high temperatures that the value of its atomic heat approximated to that demanded by Dulong and Petit's law—a fact which accounted for the discrepant conclusions of previous and subsequent workers. Nevertheless, Reynolds' prevision of the true place of glucinum in the periodic series turned out to be correct, and there is no further doubt on the subject.

Reynolds was one of the first to introduce quantitative work into the early training of the student of chemistry, thereby familiarising him experimentally with the relation between atomic weights,

equivalents, valency, etc. His "Experimental Chemistry for Junior Students," in which he developed this system, was a distinctly original work, and has had a considerable measure of success in school teaching. As his own staff was very limited, much of his time during the session was spent in doing demonstrator's work in the laboratory. In this way he acquired practical experience of the working of his system, which he incorporated in subsequent editions of his book. Indeed, he gave so much of his time and energies to his professorial duties that steady, uninterrupted research work had to be relegated to the vacations.

Probably the best known of Reynolds' contributions to organic chemistry is his discovery of thiourea. As already stated, one of his earliest contributions from the little laboratory he had established when a boy in his father's house at Booterstown was concerned with ammonium sulphocyanide. On heating this salt to a few degrees above its melting point, dissolving the product in water, and allowing the concentrated solution to stand, he obtained a substance crystallising in silky needles, the true nature of which for a time escaped him, but which he eventually characterised as an isomeride of sulphocyanogen, under which title he communicated a short paper to the *Journal* of the Royal Dublin Society. A further account appeared in the *Journal* of the Chemical Society for 1869, and was quickly re-published in various Continental periodicals. It is not often that a young man of twenty-three hits on so remarkable a discovery, and particularly one which had baffled the skill of men like Liebig and Hofmann. It at once established Reynolds' position as one of the most promising of the younger Irish chemists, and no doubt contributed greatly to his subsequent professional success. Thiourea, or thiocarbamide, as it was indifferently termed for a time, proved to be an exceedingly reactive substance, and the preparation of its derivatives and congeners, and the elucidation of their constitution, have been pre-eminently associated with the chemical laboratory of Trinity College, Dublin.

Reynolds vacated his chair in Dublin in 1903, and took up his residence in London. He continued to pursue his experimental work at the Davy-Faraday laboratory, and ultimately fitted up a small laboratory in his house. His last published communication, "On the Synthesis of a Silicalcyanide and of a Felspar," appeared in the *Proceedings* of the Royal Society in 1913. In previous papers he had given descriptions of organic compounds containing the silicocyanogen group, SiN, proving the marked affinity of silicon for tervalent nitrogen. In his last paper he gave an account of the synthesis of a silicon compound of aluminium and calcium—a

calcium silicalcyanide, $CaSi_2Al_2$, analogous to CaC_2N_2, yielding, on oxidation, a substance of the composition of anorthite, $CaAl_2Si_2O_8$, with the properties of the naturally occurring mineral. The keeper of the minerals of 1867 was, up to the last, faithful to the conceptions which had dominated nearly half a century's intellectual activity.

Reynolds joined the Chemical Society in 1873, and became a Vice-President in 1881—1884, in 1889—1892, and again in 1897—1900. In 1901—1903 he served as President. In the first of his presidential addresses he discussed, with his characteristic lucidity of exposition, the development of a subject to which he had given much thought, and with which he had been associated since the early eighties, namely, the Periodic Law. In the following year he dealt with some pressing questions of inorganic research —inorganic isomerism and the so-called inorganic ferments, in which he gave a highly suggestive summary of many problems which have since occupied the attention of many workers, and some of which have proved to be of great technical importance. He was elected into the Royal Society in 1880, served on the Council, 1900—1902, and was a Vice-President in 1901—1902. He was an original member of the Society of Chemical Industry, of which he became President in 1891, presiding over the only Annual Meeting of the Society held in Ireland. He presided over the chemical section of the British Association at the Nottingham meeting in 1893.

In 1875 he married Janet Elizabeth, the daughter of Prebendary Finlayson, of Christchurch Cathedral, Dublin, who survives him. During his later years his eyesight, never very good, gradually failed, but his mental power was active to the last. He had a serious accident in the autumn of 1919, fracturing a rib; this was followed by a slight stroke, from which he never wholly recovered. He died very suddenly on February 17th, 1920, at his residence in Kensington.

T. E. Thorpe.

WATSON SMITH.

Born June 16th, 1845; Died May 1st, 1920.

Watson Smith, who died on May 1st, 1920, was the son of the Rev. Watson Smith, and was born at Stroud in 1845. His early training in chemistry he received under Sir Henry Roscoe at Owens College, Manchester, which he entered in 1862, and had

amongst his fellow-students Sir Edward Thorpe and the late G. I. Snelus, who also commenced their chemical studies in the same year. His chemical education was continued at Heidelberg, and later on pursued at Zurich. Here Watson Smith came under the influence of Professor Lunge, and this undoubtedly proved an important factor in directing his subsequent career. After some years spent in industry, he was appointed Lecturer in Technological Chemistry in Owens College, a position he retained until 1889, and on leaving Manchester to reside in London, he became for a period the Professor of Applied Chemistry at University College. Shortly after his appointment at Owens College, the Society of Chemical Industry was founded, in 1881, and in this movement he took an active part. Of the *Journal* of this Society he became the first editor, a post he held for thirty-two years. The recognised position which this *Journal* has attained is in the main due to the care and direction it received from Watson Smith, and surely this success may be counted amongst the most important contributions to the advancement of chemistry made by him. Something of this success is to be credited to our own *Journal*, for it was as an abstractor, in fact, one of the first, that Watson Smith acquired an experience which he later turned to such useful account.

By his investigations, either alone or in collaboration with others, he contributed to various departments of chemistry, both pure and applied. In this connexion, his researches on "Diphenyl," "*iso*Dinaphthyl," "The Exhaustive Chlorination of Certain Hydrocarbons," and "Pentathionic Acid" may be cited. The chemistry of coal and of coal-tar has been materially advanced by his researches, and as far back as 1883 he directed attention to the importance of the full utilisation of coal, insisting on the necessity for the adoption of the practice of coking in retort ovens, with the recovery of the ammonia and other of the valuable by-products formed. It must have been a source of gratification to him to have seen the fruition of his advocacy, by the widespread adoption in recent years, of these methods of coking.

He was elected a Fellow of this Society in 1866, so that at the time of his death he had already passed his jubilee as a Fellow. He was an original Fellow of the Institute of Chemistry, and for two periods (1883—1887, 1888—1892) acted as an examiner for the Institute.

In music and musical composition Watson Smith found his recreation, and was a skilful executant on the piano.

He was twice married, and is survived by his second wife and children of the first marriage. P. P. B.

ALFRED WERNER.

BORN DECEMBER 12TH, 1866; DIED NOVEMBER 15TH, 1919.

THE originator of the co-ordination theory of valency and chemical constitution was born in Mulhouse in modest circumstances, his father being a factory inspector who, with the assistance of his mother (née Teché), also cultivated a small holding.

Pocket-money was scarce, and young Werner, who had already in his early school days manifested a great liking for chemistry, undertook such humble tasks as chopping wood for the neighbours in order to procure a few additional centimes wherewith to buy scientific books and chemical materials and apparatus. At eighteen years of age, having fitted up a laboratory in a barn on his father's homestead, he submitted to Professor Noelting the manuscript of his earliest chemical investigation, with the naïve inquiry as to how long it would take to become a professor. A sympathetic appreciation of the work, with a guarded reply to his question, confirmed Werner in his enthusiasm for chemistry, so that when a year later he joined the army at Karlsruhe as a one-year volunteer, he seized this opportunity of commencing his studies at the technical high school.

In later years he recalled with pleasure the circumstance that he was frequently posted as sentry before the palace wherein dwelt the Princess Victoria, afterwards Queen of Sweden, whose court he subsequently attended as Nobel prizewinner.

In 1886 Werner proceeded to Zurich, and continued his studies in the Federal Polytechnic under Professors Lunge, Hantzsch, and Treadwell. Three years later, having obtained his diploma as technical chemist, he became assistant to Lunge, at the same time working for his doctorate, under Hantzsch's guidance, on the spatial arrangement of atoms in nitrogenous compounds. In this research, which proved to be of exceptional importance, the young chemist displayed remarkable powers as an observer and original thinker.

After a short stay in Paris with Berthelot, he returned to Zurich, where his independently published memoirs on the theory of affinity and valency, and on the constitution of inorganic compounds, speedily led to his appointment, at the age of twenty-seven, as Extraordinary Professor in the University, and two years later as Ordinary Professor in succession to Victor Merz.

During these early years the Zurich laboratories were of very primitive type, and consisted largely of cellars and basements so

insufficiently lighted and ventilated that they received the ominous name of "catacombs." Yet, in spite of these material drawbacks, the master's inspiring personality attracted each year a larger band of enthusiastic students. In 1905 the Cantonal authorities acceded to the professor's strongly expressed request for more adequate accommodation, and, with the completion of the new laboratories in 1909, Werner at length became provided with an installation worthy of the epoch-making researches to which he devoted the remainder of his life.

Werner's capacity for work was prodigious: always the first to arrive at the Institute, he was frequently the last to leave it. His publications reached a total of 169, and 200 dissertations were produced by his pupils, of whom he sometimes had as many as twenty-five working simultaneously under his personal guidance. But in spite of the strenuous existence which these activities entailed, Werner, who was of a jovial disposition, found time for conviviality and for such social recreations as card-games, billiards, and chess. He delighted in bringing together under his hospitable roof his colleagues and past and present students, and of these festive gatherings he was the life and soul.

Werner had a comparatively short career of meteoric brilliancy, and the transcendant quality of his work brought him rapid recognition from scientific contemporaries throughout the world. The Swiss universities granted honorary degrees and learned societies in all lands bestowed various honorific distinctions. He was elected an Honorary and Foreign Member of the Chemical Society in 1913, and in the same year the Nobel Prize came as a culminating honour. These gratifying marks of appreciation made, however, no difference to his naturally modest demeanour, and served only to stimulate him to further efforts and more arduous toil.

In 1915, while at the pinnacle of his fame, the first insidious symptoms of his fatal malady (arteriosclerosis) declared themselves, and then followed four tragic years of increasing suffering and infirmity until death brought respite and release.

Although the time for accomplishment was short, Werner's life-work is not to be regarded as incomplete or unfinished. The co-ordination theory, which, with creative genius and prophetic insight, he had conceived as a young investigator, was before his death extended logically to its remotest consequences, and was subjected in his laboratory to the most rigid and exhaustive proofs.

Werner's success is a triumph of the inductive method of reasoning. His ideas were inborn and swiftly engendered, but he spared himself no pains to confirm these preconceptions by reference to cognate facts, or, if these were lacking, by crucial laboratory tests.

His prevision was so exact and well focussed that in the great majority of cases it was confirmed by experiment. These repeated verifications rendered Werner rather impatient of controversy, and he paid little attention to views which differed from his own; but although he felt sure that his hypotheses were correct, yet he was open-minded enough to believe that his theory was only a stepping-stone to a more comprehensive generalisation of chemical phenomena.

Though somewhat autocratic as director of research, he was, however, geniality personified to all students who sought his advice, and as a teacher his enthusiasm for his subject was contagious. An English pupil describes his lectures on inorganic chemistry and the periodic classification as "a perfect joy." His classical treatise, "Neuere Anschauungen auf dem Gebiete der anorganische Chemie," the work of several years, is a remarkable testimony to the encyclopædic character of his knowledge and comprehensive grasp of inorganic chemistry.

Organic Researches.

For several years after his promotion to the university chair, Werner divided his attention between the inorganic and organic sections of chemistry, with an ever-increasing bias towards the former. His earliest memoir, published jointly with Hantzsch, contains their celebrated hypothesis of the stereochemical configuration of the oximes. Werner followed up this idea by further researches on oximes and allied compounds, and this work on the structure of doubly linked carbon–nitrogen compounds is to be regarded as his most important contribution to organic chemistry.

Considerable attention was devoted in the Zurich school to the study of phenanthrene derivatives, which are of interest on account of their relationship to certain natural products, and Werner's discovery of xanthonium salts, together with his researches on pyronium salts, are notable contributions to our knowledge of oxonium compounds.

Inorganic Researches.

In 1891, when Werner first propounded his views on chemical affinity and valency, Kekulé's theory of constant or fixed valency, which had proved of fundamental importance in the development of organic chemistry, was more or less accepted as the guiding principle in explaining the constitution of inorganic compounds. In this respect it was not helpful, and sufficient evidence had already accumulated to show that a theory of variable valency was more in accord with known facts. Werner discarded the idea of

constant valency with a fixed number of valency units of equivalent strength operating in certain definite directions, and assumed that the chemical affinity of an element was distributed uniformly over the surface of its spherical atom in such a manner that, according to the circumstances attending chemical combination, this affinity could be divided up in a great variety of ways into few or many valency units of varying intensities. This new viewpoint of chemical affinity had its effect even in organic chemistry, where it was utilised in elucidating certain facts of aromatic substitution and of stereochemical change. But a longer stride was taken in 1893 by the publication of a dissertation on the constitution of inorganic compounds, wherein Werner expounded more explicitly his new theory of variable valency. At that time, hydrated and ammoniated simple salts, and also double salts, were formulated either as "molecular" compounds, $CaCl_2,6H_2O$, $PtCl_2,4NH_3$, $FeCl_3,3KCl$, or as open-chain complexes,

$$Ca\begin{matrix}OH_2\text{–}OH_2\text{–}OH_2\text{–}Cl\\OH_2\text{–}OH_2\text{–}OH_2\text{–}Cl\end{matrix}; \quad Pt\begin{matrix}NH_3\text{–}NH_3\text{–}Cl\\NH_3\text{–}NH_3\text{–}Cl\end{matrix}; \quad Fe\begin{matrix}Cl{=}Cl\text{–}K\\Cl{=}Cl\text{–}K\\Cl{=}Cl\text{–}K\end{matrix};$$

but neither of these methods of representation gave any clear explanation of the properties of these substances.

Co-ordination Number.

In opposition to these unsatisfactory formulations, Werner put forward his "co-ordination formulæ," according to which the associating units, OH_2, NH_3, or KCl, are grouped round a central atom, which is usually metallic. The maximum number of these groups which can find a place in the co-ordination sphere immediately surrounding the central atom is termed the "co-ordination number." The associating units implicated in a stable co-ordination complex have no ionic properties, but outside this inner or first sphere there may be ionisable radicles, as shown in the following co-ordination formulæ:

$$[Ca(OH_2)_6]Cl_2, \quad [Pt(NH_3)_4]Cl_2, \quad [FeCl_6]K_3,$$

where the co-ordination complexes or first spheres are included in square brackets.

The co-ordination complex can be produced either by the addition of elementary or compound radicles, as in the combination of platinic chloride and potassium chloride, or by the assimilation into this inner co-ordination sphere of a number of complete molecules, as in the interaction of ammonia and cobaltic chloride. The products $[PtCl_6]K_2$ and $[Co(NH_3)_6]Cl_3$ are typical respectively of two great general classes of co-ordination compounds.

Residual Affinity—Supplementary Valency.

The effective force in these combinations is the residual affinity or supplementary (auxiliary or secondary) valency of the central atom, which, although not powerful enough to attract further atoms or radicles having integral valencies, is nevertheless sufficiently intense to combine with another molecule possessing a similar degree of unsaturation.

The co-ordination complex may, however, be built up partly by the agency of principal valency and partly by that of supplementary valency, as shown in the following series, where cobalt is consistently tervalent:

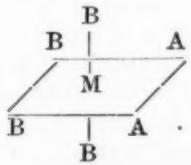
$$\left[Co(NH_3)_6\right]Cl_3 \qquad \left[Co\begin{matrix}(NH_3)_5\\Cl\end{matrix}\right]Cl_2 \qquad \left[Co\begin{matrix}(NH_3)_4\\Cl_2\end{matrix}\right]Cl$$
$$\left[Co\begin{matrix}(NH_3)_3\\Cl_3\end{matrix}\right].$$

The gradual introduction of chlorine into the complex is accompanied by a diminution in the electrical conductivity of the compound; the fourth member, which contains all the chlorine in the inner sphere, is practically a non-electrolyte.

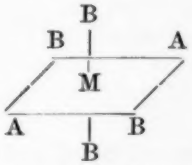
In the majority of cases, the co-ordination number is six, but with carbon, boron, glucinum, and bivalent platinum it is four, and it increases to eight for molybdenum, tungsten, and a few other elements.

Geometrical Isomerism.

The frequent recurrence of the co-ordination number six suggested a definite spatial grouping of the associating units. Three arrangements present themselves: the hexagon, the triangular prism, and the regular octahedron. If either of the first two arrangements be assumed, a co-ordination complex of the type $[MA_2B_4]$ should exist in three isomeric forms, corresponding with the three di-substituted isomerides of the hexagonal and prismatic constitutions of benzene, but if the associating groups A_2B_4 are situated at the vertices of a regular octahedron, then only two stereoisomerides are possible:



cis- or 1 : 2-form.



trans- or 1 : 6-form.

Many compounds of this type were examined, of which no fewer than twenty-seven series contained cobalt as central atom, and in every case only two stereoisomerides were detected. In most instances the stereochemical configuration of each isomeride was established by taking advantage of the fact that, as in organic chemistry, only the *cis*-position lends itself readily to ring formation.

Inorganic and Co-ordination Isomerism.

The demonstration of several other types of inorganic isomerism furnished additional confirmation of the co-ordination theory and of the important part played by the co-ordination complex.

Hydrate isomerism was shown in the following series of salts, which differed considerably in physical and chemical properties:

$[Cr(OH_2)_6]Cl_3$; $[Cr(OH_2)_5Cl]Cl_2,H_2O$; $[Cr(OH_2)_4Cl_2]Cl,2H_2O$.
Blue. Green. Green.

Several other more complicated cases of hydrate isomerism were discovered by Werner and his collaborators.

Ionisation isomerism was exemplified by such examples as the following pair, containing, respectively, nitrite and chlorine ions:

$$\left[\begin{matrix}Cl\\NO_2\end{matrix}\ Co\,en_2\right]NO_2 \qquad [(NO_2)_2\,Co\,en_2]Cl.$$

Salt isomerism, arising from the circumstance that the nitrite and thiocyanate groups often present in the co-ordination complexes can each exist in two differently constituted forms, is exemplified by the following compounds, where "en" represents ethylenediamine, a molecule of which often replaces two molecules of ammonia, thus occupying two positions in the co-ordination complex:

$$\left[\begin{matrix}ONO\\ONO\end{matrix}\ Co\,en_2\right]X \qquad \left[\begin{matrix}O_2N\\O_2N\end{matrix}\ Co\,en_2\right]X$$
Labile. Stable,

Co-ordination position isomerism is possible owing to the fact that associating units maintain a definite spatial orientation, even in highly complex structures, such as the following:

$$\left[\begin{matrix}Cl\\(NH_3)_3\end{matrix}\ Co\begin{matrix}NH_2\\-O_2-\end{matrix}Co\ \begin{matrix}Cl\\(NH_3)_3\end{matrix}\right]Cl_2$$

$$\left[(NH_3)_4\,Co\begin{matrix}NH_2\\-O_2-\end{matrix}Co\ \begin{matrix}Cl_2\\(NH_3)_2\end{matrix}\right]Cl_2$$

Many other series of a highly complicated character containing two or more metallic atoms were examined by Werner and his

pupils, and shown to conform to the fundamental principles of the co-ordination theory.

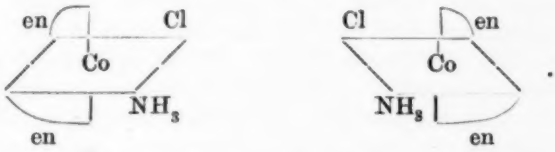
The culminating point in these researches was reached with the discovery of optical isomerism among co-ordination compounds.

Octahedral Enantiomorphism.

Object. Mirror-image.

Geometrical isomerides of the *cis*-series having the general formulæ $[MA_2\,en_2]X$ and co-ordination compounds of the type $[M\,en_3]X_3$ containing, respectively, two and three molecules of ethylenediamine should each exist in two optically active enantiomorphous forms corresponding with the foregoing general formulæ, in which the central atom is surrounded by a complex consisting of at least two ethylenediamine molecules or similar caliper-like groups.

After many disappointments, the resolution of 1 : 2-chloroammino-diethylenediamine cobaltic chloride, $\left[\begin{matrix}NH_3\\Cl\end{matrix}Co\,en_2\right]Cl_2$, was accomplished in 1911 with the aid of *d*-bromocamphorsulphonic acid.



This striking confirmation of Werner's views of the configuration of co-ordination compounds was speedily followed by other analogous resolutions, and optically active compounds of octahedral symmetry are now known containing cobalt, chromium, iron, iridium, platinum, rhodium, and ruthenium as central metallic atoms.

Considerable ingenuity was displayed in the selection of these co-ordination compounds, and, out of the many examined, two may be mentioned as being of outstanding interest. The well-known blue double potassium chromium oxalate, $[Cr(C_2O_4)_3]K_3$, and the remarkable red additive compound of ferrous bromide and αα-dipyridyl, $[Fe(Dip)_3]Br_2$, were successfully resolved, and thus shown to possess octahedral symmetry.

More than forty series of these compounds of octahedral symmetry have been shown to exist in optically active forms, so that the spatial configuration of the co-ordination complex with six associating units is now as firmly established as that of the asymmetric tetrahedral carbon atom.

Werner's activities did not, however, abate even with this complete and crowning demonstration. The search for further evidence was extended in all directions. The polynuclear complexes with two cobalt atoms, which should, in accordance with the theory, display remarkable optical properties, were put to the test, and found to confirm Werner's theoretical anticipations in every particular. Among these may be cited the case of the following complex salt, $\left[\text{en}_2\text{Co}\begin{matrix}\cdot\text{NO}_2\cdot\\ \cdot\text{NH}_2\cdot\end{matrix}\text{Co en}_2\right]\text{X}_4$, which was shown to exist in four modifications: two optically active forms, a racemic form, and an optically inactive form, due to internal compensation. Accordingly, these four varieties of the substance furnish a complete analogy to the four tartaric acids. This binuclear co-ordination compound illustrates also an important corollary of the co-ordination theory, the smoothing out and equalisation of the difference between principal and supplementary valencies (ionogenic and non-ionogenic valencies) within the co-ordination complex. The existence of an internally compensated analogue of mesotartaric acid shows that the bridging groups NO_2 and NH_2, although originally attracted into the co-ordination complex partly by principal and partly by supplementary valency, are now similarly associated with each of the two cobalt atoms.

The optically active co-ordinated compounds hitherto considered contain carbon present in the ethylenediamine or $\alpha\alpha$-dipyridyl molecules or in oxalate complexes. In order, however, to remove any lurking suspicion that carbon may, after all, be even a contributory cause of the optical activity in these substances, Werner (1914) resolved a purely inorganic compound entirely free from carbon. In this substance the basic cobaltic complex, $[Co(NH_3)_4(OH)_2]X$, took the place of ethylenediamine, and three molecules were co-ordinated with cobaltic bromide. The resulting complex bromide, $\left[\text{Co}\begin{Bmatrix}\text{OH}\\ \text{OH}\end{Bmatrix}\text{Co}(\text{NH}_3)_4\right\}_3\Big]\text{Br}_6,2\text{H}_2\text{O}$, was resolved successfully through the bromocamphor-π-sulphonates into optically active components, thus proving beyond all doubt that this form of optical isomerism is not due to the presence of any special element or group of elements, but is simply a geometrical property of the octahedral co-ordination complex.

Applications of the Co-ordination Theory.

Numerous resolutions of octahedral racemoid substances, made with the aid of organic optically active compounds, tartaric acid, camphorsulphonic acid, bromocamphorsulphonic acid, nitrocamphor, and the alkaloids, placed Werner in possession of many optically active products of octahedral symmetry. These new reagents were promptly applied to refractory racemoid substances of tetrahedral symmetry and, in the resolution of *s*-dimethylsuccinic acid with the aid of the optically active triethylenediamine cobaltic bromides, [Co 3en]Br_3, Werner (1913) repaid the debt he owed to Pasteur.

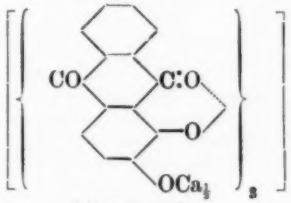
The acceptance of Werner's theory by other investigators has led to the study of co-ordination compounds of very diverse types. Among these are several which have already proved useful in chemical analysis, such as the metallic derivatives of dimethylglyoxime, benzildioxime, dicyanodiamidine, nitroso-β-naphthol, and phenylnitrosohydroxylamine (cupferron).

The theory offers a valid explanation of the constitution of many complex minerals, for instance, atacamite (I) and its analogues, and the members of the apatite group (II), where M = Ca or Pb,

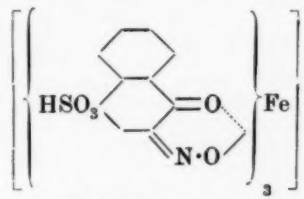
$$[Cu\{Cu(OH)_2\}_3]Cl_2 \quad (I.) \qquad [M\{M_3(RO_4)_2\}_3]X_2. \quad (II.)$$

R = P, As or V, and X = F or Cl, may be formulated as co-ordinated compounds. In this connexion, it should be mentioned that the co-ordination theory has widened considerably, and, at the same time, rendered more precise our conceptions of isomorphism.

An extension of the theory to which Werner paid considerable attention was its general explanation of the mechanism of adjective dyeing with metallic mordants. The resulting highly-coloured lakes, to which the tinctorial effect is due, have the characteristic properties of internally co-ordinated complexes: insolubility, exceptional colour, chemical inertness, and an inhibition of the ordinary analytical properties of the metallic atom. It is impossible to summarise this rapidly growing section of co-ordination chemistry, but two typical examples may be formulated.



Alizarin-red.



Naphthol-green G.

At least one important metallurgical industry—the production of pure nickel—may, in the light of this theory, be regarded as being dependent on the singular properties of a co-ordination complex, nickel carbonyl.

Werner's generalisation has all the attributes of a scientific theory of first-rate importance. It is in close accordance with known facts, which it explains and summarises in a logical and comprehensive manner. It endows its exponents with the gift of prophesy, and many far-reaching predictions based on its simple hypotheses have been subsequently verified by direct experiment.

By birth Werner was an Alsatian subject of the second French Empire, but with the annexation of his native province by Germany in 1871, his nationality became changed, and, as already narrated, he served in the German army. His early studies in Zurich imbued him, at an impressionable age, however, with a love for the democratic institutions of Switzerland. The call to a Swiss chair of chemistry strengthened this bond, and in 1895, the year of his marriage to a lady of Zurich (Fräulein Emma Giesker), Werner became by naturalisation a citizen of the Swiss Confederation. Thenceforward he became wholeheartedly a Swiss, remaining attached to Zürich and loyal to his adopted fatherland in spite of gratifying invitations to Vienna and to Würzburg. He spoke German intentionally with a Swiss accent, and took great pride in displaying a colloquial knowledge of the local *patois*. Werner's deliberate change of nationality was for him a happy choice, for while neighbouring empires were tottering to their fall in a turmoil of war and social unrest, the alpine republic gave to her illustrious adherent one of the greatest of earthly blessings, peace: for the fulfilment of his life's work and in his closing years.

The writer's best thanks are extended to Professors Fierz, Karrer, and Staudinger, and to Mr. C. W. Bailey, for their kind assistance in the compilation of this memoir.

G. T. Morgan.

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FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus **5 IV** indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

C_1 Group.

CH_4 Methane, ignition of mixtures of air and (MASON and WHEELER), 36, 1227; (WHEELER), 903; propagation of flame in mixtures of oxygen, nitrogen, and (PAYMAN), 48; action of chlorine with, under the influence of light (WHISTON), 183.

CO_2 Carbon dioxide, pure, preparation of (FARMER), 1446.

1 II

CHN Hydrocyanic acid, mercuric salt, action of, on metallic salts (GUPTA), 67; nickel salt, preparation of (GUPTA), 69.

CH_3Cl Methyl chloride, conversion of, into methyl alcohol and methyl acetate (WHISTON), 183.

CH_4O Methyl alcohol, synthesis of, from methyl chloride (WHISTON), 183.

CH_5N Methylamine, preparation of, from ammonium methyl sulphate (DENHAM and KNAPP), 236.

CH_5N_3 Guanidine, preparation of (WERNER and BELL), 1133.

CO_8N_4 Tetranitromethane, preparation and properties of (ORTON and MCKIE), 294; effect of reducing agents on, and a rapid method of its estimation (BAILLIE, MACBETH, and MAXWELL), 880.

1 III

CHON Cyanic acid, constitution of, and the formation of urea from its interaction with ammonia (WERNER and FEARON), 1356.

CHO_6N_3 Nitroform, estimation of, with potassium permanganate (MCKIE), 646.

CHNS Thiocyanic acid, metallic salts, compounds of hydrazine with (RÂY and SARKAR), 321; ammonium salt, interaction of dicyanodiamide and (WERNER and BELL), 1133.

CH_3O_2N Methyl nitrite, preparation of (SLATER), 588.

CH_4ON_2 Carbamide, mechanism of the synthesis of (WERNER), 1046; decomposition of (WERNER), 1078.

$COCl_2$ Carbonyl chloride, preparation and physical properties of (ATKINSON, HEYCOCK, and POPE), 1410.

C_2 Group.

C_2H_2 Acetylene, action of nitric acid on (ORTON and MCKIE), 283.

C_2H_4 Ethylene, interaction of selenium chloride and (BAUSOR, GIBSON, and POPE), 1453.

2 II

$C_2H_4N_4$ Dicyanodiamide, interaction of ammonium thiocyanate and (WERNER and BELL), 1133.

C_2H_5I Ethyl iodide, preparation of (HUNT), 1592.

C_2H_6O Ethyl alcohol, surface tension of mixtures of water and (FIRTH), 268; equilibrium in the system: benzene, water, and (SIDGWICK and SPURRELL), 1397; action of, on sodium sulphates (BUTLER and DUNNICLIFF), 649.

$C_2H_8N_2$ α-Amino-α-iminoethane, and its salts (FARGHER), 674.

C_2H_6Te Methyl telluride (VERNON), 892.

2 III

$C_2H_3O_2Cl$ Chloroacetic acid, preparation of esters of, by means of αβ-dichlorovinyl ethyl ether (CROMPTON and VANDERSTICHELE), 691.

C_2H_5OCl Chloromethyl ether, syntheses by means of (SIMONSEN), 564.

C_2H_5OBr Ethylenebromohydrin, preparation and characterisation of (READ and HOOK), 1214.

$C_2H_5Cl_2As$ Ethyldichloroarsine (MCKENZIE and WOOD), 407.

C_2H_6OTe Dimethyltelluronium oxide, and its silver salt (VERNON), 94, 889.

$C_2H_6O_2Te$ Dimethyltellurone, preparation of (VERNON), 894.

$C_2H_6Cl_2Te$ Dimethyltelluronium dichlorides (VERNON), 98.

$C_2H_6Br_2Te$ Dimethyltelluronium dibromides (VERNON), 96.

C_2H_6IAs Dimethyliodoarsine, preparation of (BURROWS and TURNER), 1376.

$C_2H_6I_2Te$ Dimethyltelluronium di-iodides (VERNON), 90.

$C_2H_7ON_3$ Methylsemicarbazides, and their oxalates (FORSTER and SAVILLE), 759.

$C_2H_8O_2Te$ Dimethyltelluronium dihydroxide (VERNON), 897.

2 IV

$C_2H_5OCl_2As$ Ethoxydichloroarsine (MCKENZIE and WOOD), 406.

C_3 Group.

$C_3H_4O_4$ Malonic acid, rate of decomposition of (HINSHELWOOD), 156.

$C_3H_5N_3$ Aminoglyoxaline, dipicrate of (FARGHER), 673.

$C_3H_6O_2$ Methyl acetate, synthesis of, from methyl chloride (WHISTON), 183.

3 III

C_3H_3ON Cyanoacetamide, condensation of aldehydes with (DAY and THORPE), 1465.

$C_3H_5O_2Cl$ Ethyl chloroformate, action of pyridine and quinoline with (HOPKINS), 278.

C_3H_9ITe Trimethyltelluronium iodide, preparation of (VERNON), 894.

3 IV

$C_3H_4O_3N_2S$ Glyoxalinesulphonic acid, and its salts (PYMAN and RAVALD), 1430.

C_4 Group.

$C_4H_6O_6$ r-Tartaric acid, resolution of, by means of l-borneol (WREN, WILLIAMS, and MYDDLETON), 191.

$C_4H_7N_3$ 4-Amino-5-methylglyoxaline, and its salts (FARGHER), 675.

C_4H_8O n-Butaldehyde, condensations of (WEIZMANN and GARRARD), 324.

$C_4H_{10}O$ n-Butyl alcohol, condensations of (WEIZMANN and GARRARD), 324.

$C_4H_{12}N_3$ Diethylenetriamine, and its salts (FARGHER), 1351.

4 III

$C_4H_6OCl_2$ αβ-Dichlorovinyl ethyl ether, preparation of, and its synthetic uses (CROMPTON and VANDERSTICHELE), 691.

$C_4H_8Cl_4S$ $\beta\beta'$-Dichlorodiethyl sulphide (GIBSON and POPE), 271 ; syntheses with (DAVIES), 297 ; estimation of, volumetrically (HOLLELY), 898.
$C_4H_8Cl_4Se$ $\beta\beta'$-Dichloroethyl selenide dichloride (BAUSOR, GIBSON, and POPE), 1454.
C_4H_9NS 1:4-Thiazan, and its sa[illegible] (DAVIES), 306.
$C_4H_{12}O_2Te$ Dimethyltelluronium dimethoxide (VERNON), 897.
$C_4H_{12}NI$ Tetramethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1312.

4 IV

$C_4H_8OCl_2S$ $\beta\beta'$-Dichloroethyl sulphoxide (GIBSON and POPE), 277.
$C_4H_8O_5N_2S$ Carbomethoxy-ψ-thiocarbamide bicarbonate (DIXON and KENNEDY), 85.
$C_4H_{10}O_2ClAs$ Diethoxychloroarsine (MCKENZIE and WOOD), 407.

4 V

$C_4H_7O_2N_2Cl_3S$ Thiocarbamide methyl trichloroacetate (TAYLOR), 10.
$C_4H_9O_3N_2Cl_2S$ Thiocarbamide methyl dichloroacetate (TAYLOR), 10.
$C_4H_9O_3N_2ClS$ Methyl *iso*thiohydantoate hydrochloride (TAYLOR), 9.
Thiocarbamide methyl chloroacetate (TAYLOR), 7.
$C_4H_{17}ON_4Cl_2Co$ *trans*-Dichlorodiethylene diaminecobaltic hydroxide, salts of (PRICE and DUFF), 1075.

C_5 Group.

C_5H_5N Pyridine, action of ethyl chloroformate on (HOPKINS), 278.

5 III

$C_5H_4O_2Te$ Tellurium acetylacetone (MORGAN and DREW), 1464.
$C_5H_9O_2Cl$ *n*-Butyl chloroformate (CHATTAWAY and SAERENS), 708.
$C_5H_{11}O_2N$ *n*-Butyl carbamate (CHATTAWAY and SAERENS), 709.

5 IV

$C_5H_6O_2Cl_2Te$ Tellurium acetylacetone dichloride (MORGAN and DREW), 1462.
$C_5H_6O_3N_2S$ Carbomethoxy *iso*thiohydantoin (DIXON and KENNEDY), 79.
$C_5H_8O_4N_2S$ Dicarbomethoxythiocarbamide (DIXON and KENNEDY), 85.

5 V

$C_5H_{10}O_5N_2S$ Carbethoxy-ψ-thiocarbamide bicarbonate (DIXON and KENNEDY), 83.
$C_5H_{11}O_2N_2ClS$ Thiocarbamide ethyl chloroacetate (TAYLOR), 10.
$C_5H_{19}O_7N_4S_2Co$ *cis*-Methionatodiethylenediaminecobaltic hydroxide, salts of (PRICE and DUFF), 1073.

5 VI

$C_5H_{16}O_6N_4BrS_2Co$ *cis*-Methionatodiethylenediaminecobaltic bromide ($+ 2H_2O$) (PRICE and DUFF), 1073.

C_6 Group.

C_6H_6 Benzene, influence of drying agents on the freezing point of (SIDGWICK), 1340 ; equilibrium in the system : ethyl alcohol, water, and (SIDGWICK and SPURRELL), 1397.

6 II

$C_6H_{10}O_3$ Ethyl acetoacetate, condensation of, with *p*-dimethylaminobenzaldehyde and ammonia (HINKEL and CREMER), 137.
$C_6H_{12}O_3$ Methyl *n*-butyl carbonate (CHATTAWAY and SAERENS), 709.
$C_6H_{12}O_6$ Fructose, relationship of inulin to (IRVINE and STEELE), 1474.
Glucose, conversion of cellulose into (IRVINE and SOUTAR), 1489.
$C_6H_{12}S_3$ Triethylene trisulphide (RÂY), 1090.

$C_6H_{12}S_4$ Triethylene tetrasulphides (Ray), 1090.
$C_6H_{14}S_4$ Triethylene disulphide dimercaptan (Ray), 1092.
$C_6H_{18}N_4$ Triethylenetetramine, and its salts (Fargher), 1354.

6 I

$C_6H_5I_2As$ Phenyldi-iodoarsine (Burrows and Turner), 1376.
$C_6H_7ON_3$ *N*-Nitroso-β-phenylhydroxylamine, ammonium salt (*cupferron*), preparation of (Slater), 591.
$C_6H_5O_3N$ Nitropaenol, preparation of (Rennie, Cooke, and Finlayson), 342.
$C_6H_{16}O_2N_2$ Methylammonium diethylcarbamate (Werner), 1052.

6 IV

$C_6H_5O_2N_2B$ Nitrosoboranilide (Chaudhuri), 1082.
C_6H_6ONB Boranilide, and its salts (Chaudhuri), 1082.
C_6H_6NSB Thioboranilide (Chaudhuri), 1083.
$C_6H_8O_2N_2S$ Carbethoxy*iso*thiohydantoin, and its hydrochloride (Dixon and Kennedy), 78.
$C_6H_{12}Cl_2S_4Hg_3$ Dichloromercaptide from triethylene disulphide dimercaptan and mercuric chloride (Rây), 1092.
$C_6H_{14}NIS$ 1:4-Thiazan ethiodide (Davies), 308.

6 V

C_6H_5ONBrB Bromoboranilides (Chaudhuri), 1082.
$C_6H_{19}O_6N_4SCo$ *cis*-Sulphoacetatodiethylenediaminecobaltic hydroxide, salts of (Price and Duff), 1072.

6 VI

$C_6H_{18}O_5N_4BrSCo$ *cis*-Sulphoacetatodiethylenediaminecobaltic bromide (Price and Duff), 1072.

C_7 Group.

C_7H_{12} Heptadiene, from *n*-butyl alcohol, acetone, and aluminium oxide (Weizmann and Garrard), 337.
C_7H_{14} Hydrocarbon from *n*-butyl alcohol, acetone, and aluminium oxide (Weizmann and Garrard), 337.

7 II

$C_7H_2Br_6$ Pentabromobenzyl bromide (Dhar), 996.
$C_7H_6O_2$ Benzoic acid, volatility of, and its derivatives in steam (Sidgwick), 396.
$C_7H_8O_2$ Guaiacol, arsinic acids derived from (Fargher), 865.
C_7H_9N Methylaniline, cadmi- and cobalto-chlorides of (Reilly and Hickinbottom), 130.
$C_7H_{10}O_3$ *cyclo*-Pentylideneacetic acid (Becker and Thorpe), 1583.
$C_7H_{10}O_4$ *trans*-Caronic acid, preparation of, and its silver salt (Simonsen), 577; (Farmer and Ingold), 1372.
$C_7H_{12}O$ Δγ-Heptylene-β-one (Weizmann and Garrard), 335.
Suberone, preparation of (Day, Kon, and Stevenson), 642.
$C_7H_{12}O_6$ αα-Dihydroxy-ββ-dimethylglutaric acid, preparation of (Farmer and Ingold), 1371.
$C_7H_{14}O_3$ Ethyl *n*-butyl carbonate (Chattaway and Saerens), 709.

7 III

$C_7H_3OBr_5$ Pentabromobenzyl alcohol (Dhar), 997.
$C_7H_5O_6N_3$ 2:3:6-Trinitrotoluene, preparation of (Drew), 1615; synthesis of (Brady and Taylor), 876.
Trinitrotoluenes, preparation of (Brady and Williams), 1137.

$C_7H_5O_8N_5$ Trinitrophenylmethylnitroamine (*tetryl*), velocity of decomposition of (FARMER), 1603; action of amines on (JAMES, JONES, and LEWIS), 1273.

$C_7H_6O_4N_2$ Dinitrotoluenes, preparation of (BRADY and WILLIAMS), 1137; action of ammonia and sodium methoxide on (KENNER and PARKIN), 852.

3-Nitroanthranilic acid, preparation of (JAMES, KENNER, and STUBBINGS), 775.

$C_7H_6O_5N_2$ 2:6-Dinitro-*m*-cresol (DREW), 1618.

$C_7H_6O_6N_4$ 2:4:5-Trinitromethylaniline (SWANN), 3.

$C_7H_6N_2Cl$ Chlorotolylenediazoimines (MORGAN and DREW), 789.

$C_7H_7O_4N_3$ 5:6-Dinitro-*o*-toluidine (BRADY and TAYLOR), 879.

Dinitrotoluidines, preparation and separation of (BRADY and WILLIAMS), 1138.

C_7H_8ClAs Phenylmethylchloroarsine (BURROWS and TURNER), 1377.

C_7H_8IAs Phenylmethyliodoarsine, preparation of (BURROWS and TURNER), 1377.

$C_7H_9O_5As$ Hydroxymethoxyphenylarsinic acids, and their calcium salts (FARGHER), 872.

$C_7H_9N_2Cl$ Chlorotolylenediamines (MORGAN and DREW), 786.

$C_7H_{21}NI$ Methyltriethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1313.

7 IV

$C_7H_4O_2N_3Cl$ 4-Chloro-7-nitroindazole (MORGAN and DREW), 787.

$C_7H_4O_4NI$ 2-Iodo-3-nitrobenzoic acid, preparation of (JAMES, KENNER, and STUBBINGS), 776.

$C_7H_5O_3NBr_2$ Dibromohydroxybenzaldoximes (WENTWORTH and BRADY), 1042.

$C_7H_5O_4N_2Cl$ Chlorodinitrotoluenes (MORGAN and DREW), 786.

$C_7H_7O_2N_2Cl$ Chloronitrotoluidines (MORGAN and DREW), 787.

$C_7H_8O_6NAs$ 3-Nitro-4-methoxyphenylarsinic acid, and its sodium salt (FARGHER), 868.

$C_7H_8O_7NAs$ Nitrohydroxymethoxyphenylarsinic acids (FARGHER), 871.

$C_7H_{10}O_4NAs$ 3-Amino-4-methoxyphenylarsinic acid (FARGHER), 869.

$C_7H_{12}O_4N_2S$ Dicarbethoxythiocarbamide (DIXON and KENNEDY), 83.

7 V

$C_7H_5O_2NClI$ 5-Chloro-4-iodo-3-nitrotoluene (JAMES, KENNER, and STUBBINGS), 776.

$C_7H_{18}O_4N_4BrCo$ *cis*-Malonatodiethylenediaminecobaltic bromide (PRICE and DUFF), 1076.

C_8 Group.

$C_8H_6O_5$ Anhydro-acids from carboxymethane-II$^{1:3}$-3-methyl*cyclo*propane-1:2-dicarboxylic acids (BEESLEY and THORPE), 613.

$C_8H_8O_6$ Lactone of hydroxycarboxymethane-II$^{1:3}$-3-methyl*cyclo*propane-1:2-dicarboxylic acid (BEESLEY and THORPE), 616.

Methylmethane-III$^{1:2:3}$-*cyclo*propane-1:2:3-tricarboxylic acid, and its silver salt (BEESLEY and THORPE), 617.

Tri-lactone of $\alpha\beta\beta$-trihydroxydimethylpropanetricarboxylic acid, and its silver salt (BEESLEY and THORPE), 618.

$C_8H_7Cl_3$ 3:5:6-Trichloro-*o*-xylene (HINKEL), 1300.

$C_8H_8O_3$ Fisetol (*ω-hydroxyresacetophenone*), synthesis of derivatives of (SLATER and STEPHEN), 309.

$C_8H_8O_4$ Phloroacetophenone (SEN and GHOSH), 61.

$C_8H_8O_6$ Carboxymethane-II[1:3]-3-methyl*cyclo*propane-1:2-dicarboxylic acids and their salts (BEESLEY and THORPE), 612.

Dilactone of $\beta\beta$-dihydroxydimethylpropanetricarboxylic acid (BEESLEY and THORPE), 612.

$C_8H_6Cl_2$ 2:ω(4)-Dichloro-*p*-xylene (STEPHEN, SHORT, and GLADDING), 524.

$C_8H_8Cl_5$ 2:3:3:4:5-Pentachloro-1:1-dimethyl-Δ^5-*cyclo*hexene (HINKEL), 1299.

$C_8H_{10}O_2$ Veratrole, arsinic acids derived from (FARGHER), 865.

$C_8H_{10}Cl_2$ 3:5-Dichloro-1:1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene, action of chlorine on (HINKEL), 1296.

$C_8H_{11}As$ Phenyldimethylarsine, preparation of (BURROWS and TURNER), 1378.

$C_8H_{12}O_3$ β-Propylglutaric anhydride (DAY and THORPE), 1472.

$C_8H_{12}O_6$ $\beta\beta$-Dihydroxydimethylpropanetricarboxylic acid, and its silver salt (BEESLEY and THORPE), 612.

$C_8H_{14}O$ α-Ethyl-Δ^α-hexenealdehyde (WEIZMANN and GARRARD), 329.

$C_8H_{14}O_4$ β-Propylglutaric acid, and its silver salt (DAY and THORPE), 1471.

Suberic acid, preparation of (DAY, KON, and STEVENSON), 641.

$C_8H_{16}O_2$ α-Ethylhexoic acid, preparation of (WEIZMANN and GARRARD), 330.

$C_8H_{16}O_3$ *n*-Propyl *n*-butyl carbonate (CHATTAWAY and SAERENS), 709.

$C_8H_{18}O$ α-Ethylhexyl alcohol, preparation of (WEIZMANN and GARRARD), 329.

8 III

$C_8H_5O_4I$ 2-Iodo*iso*phthalic acid, preparation of (JAMES, KENNER, and STUBBINGS), 774.

$C_8H_5O_5Br$ Bromo-anhydro-acid from bromocarboxymethane-II[1:3]-3-methyl*cyclo*propane-1:2-dicarboxylic acid (BEESLEY and THORPE), 615.

$C_8H_6Cl_3Br$ 3:4:5-Trichloro-6-bromo-*o*-xylene (HINKEL), 1300.

$C_8H_7O_6Br$ Bromocarboxymethane-II[1:3]-3-methyl*cyclo*propane-1:2-dicarboxylic acids (BEESLEY and THORPE), 615.

$C_8H_8O_5N_2$ 2:6-Dinitro-*m*-tolyl methyl ether (DREW), 1618.

$C_8H_9O_2N_3$ 3-Cyano-2:6-diketo-4-methylpiperidine-5-carboxylamide (DAY and THORPE), 1470.

$C_8H_9O_4N_3$ α- and β-Dinitrodimethylanilines (SWANN), 2.

$C_8H_{10}O_2N_4$ $\alpha\alpha'$-Dicyano-β-methylglutaramide and 6-Imino-3-cyano-5-carbamyl-4-methyl-2-piperidone (DAY and THORPE), 1469.

$C_8H_{11}O_3N$ 4-Aminoveratrole, preparation of (FARGHER), 869.

$C_8H_{11}O_5As$ 3:4-Dimethoxyphenylarsinic acid (FARGHER), 870.

$C_8H_{12}N_2S_2$ Nitrile, from potassium cyanide and $\beta\beta'$-dichlorodiethyl sulphide (DAVIES), 305.

$C_8H_{14}O_4S$ γ-Thiodibutyric acid (DAVIES), 301.

$C_8H_{14}O_4S_2$ Acid, from hydrolysis of nitrile $C_8H_{12}N_2S_2$ (DAVIES), 305.

$C_8H_{15}ON_3$ $\Delta\gamma$-Heptylene-β-one semicarbazone (WEIZMANN and GARRARD), 335.

$C_8H_{21}NI$ Tetraethylammonium iodide, mercuri-iodides of, and their crystallography (BARKER and PORTER), 1313.

8 IV

$C_8H_6O_3NCl_3$ 3:4:5-Trichloro-6-nitro-*o*-xylene (HINKEL), 1301.

$C_8H_8O_3NCl$ Chloronitroxylenes (STEPHEN, SHORT, and GLADDING), 524.

$C_8H_8O_3NBr$ 5-Bromo-*o*-methoxybenzaldoxime, and its hydrochloride (WENTWORTH and BRADY), 1043.

$C_8H_{10}OClAs$ Phenylethoxychloroarsine (MCKENZIE and WOOD), 410.

$C_8H_{10}O_7NAs$ 5-Nitro-3:4-dimethoxyphenylarsinic acid, and its salts (FARGHER), 870.

$C_8H_{12}O_5NAs$ 5-Amino-3:4-dimethoxyphenylarsinic acid (FARGHER), 871.

C_9 Group.

C_9H_7N Quinoline, action of ethyl chloroformate on (HOPKINS), 278.

$C_9H_8O_2$ Methylcoumaranones, preparation of (HIGGINBOTHAM and STEPHEN), 1541.

$C_9H_{10}O_3$ Mandelic acid, racemisation of esters of (MCKENZIE and WREN), 685.

Tolyloxyacetic acids, preparation of, and their salts (HIGGINBOTHAM and STEPHEN), 1534.

$C_9H_{10}O_4$ ω-Methoxyresacetophenone (SLATER and STEPHEN), 312.

Substance from the resin of *Xanthorrhœa* (RENNIE, COOKE, and FINLAYSON), 343.

$C_9H_{16}O_5$ Dimethyl*dicyclo*pentanonedicarboxylic acid, oxidation of (FARMER and INGOLD), 1371.

Syringic acid (ALIMCHANDANI and MELDRUM), 967.

2:4:6-Trihydroxy-ω-methoxyacetophenone ($+H_2O$) (SLATER and STEPHEN), 316.

$C_9H_{12}O_4$ Lactone of α-hydroxy*cyclo*pentane-1:1-diacetic acid (BECKER and THORPE), 1586.

cis- and *trans-cyclo*Pentane*spirocyclo*propane-1:2-dicarboxylic acids, and the silver salt of the latter (BECKER and THORPE), 1587.

$C_9H_{12}O_5$ Lactonic acid of αα′-dihydroxy*cyclo*pentane-1:1-diacetic acid (BECKER and THORPE), 1585.

$C_9H_{12}N_2$ *as*-Phenylallylhydrazine (SINGH), 1212.

$C_9H_{13}As$ Phenylmethylethylarsine (BURROWS and TURNER), 1380.

$C_9H_{14}O_5$ α-Hydroxy*cyclo*pentane-1:1-diacetic acid, silver salt (BECKER and THORPE), 1587.

$C_9H_{14}N_2$ *as*-Phenyl-α-propylhydrazine, and its hydroferrocyanide (SINGH), 1206.

$C_9H_{18}O_6$ Trimethyl γ-fructose (IRVINE and STEELE), 1485.

Trimethyl glucose (HAWORTH), 207.

9 III

$C_9H_7O_3N$ *o*-Nitrocinnamaldehyde, preparation of (MILLS and EVANS), 1037.

$C_9H_7O_6N_3$ Acetyl derivative of 2:4-dinitrobenzaldoxime (WENTWORTH and BRADY), 1042.

$C_9H_5O_7N_4$ 2:4:6-Trinitroaceto-*m*-toluidide (COOK and BRADY), 750.

C_9H_9ON Tolyloxyacetonitriles (HIGGINBOTHAM and STEPHEN), 1540.

$C_9H_9O_2N$ 5-Hydroxy-1-methylcoumaran-2-one (SLATER and STEPHEN), 317.

$C_9H_9O_2Cl$ Tolyloxyacetyl chlorides (HIGGINBOTHAM and STEPHEN), 1538.

$C_9H_9O_5N_3$ Dinitroaceto-*o*-toluidides (BRADY and TAYLOR), 879.

Dinitroaceto-*m*-toluidides (COOK and BRADY), 752.

$C_9H_{11}ON$ *p*-Dimethylaminobenzaldehyde, condensation of ethyl acetoacetate and ammonia with (HINKEL and CREMER), 137.

$C_9H_{11}O_2N$ Tolyloxyacetamides (HIGGINBOTHAM and STEPHEN), 1539.

$C_9H_{11}O_3N_3$ 3-Cyano-2:6-diketo-4-ethylpiperidine-5-carboxylamide (DAY and THORPE), 1471.

$C_9H_{11}O_6As$ Acetoxymethoxyphenylarsinic acids (FARGHER), 872.

$C_9H_{12}O_2N_4$ αα′-Dicyano-β-ethylglutaramide (DAY and THORPE), 1470.

6-Imino-3-cyano-5-carbamyl-4-ethyl-2-piperidone (DAY and THORPE), 1471.

$C_9H_{12}O_3S$ Mesitylenesulphonic acid, preparation of (GIBSON), 949.

$C_9H_{12}O_4Br_2$ *aa'*-Dibromo*cyclo*pentane-1:1-diacetic acid (BECKER and THORPE), 1585.

$C_9H_{14}NI$ Phenyltrimethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1316.

$C_9H_{14}I_2As_2$ Substance, from phenyldimethylarsine and methyldi-iodoarsine (BURROWS and TURNER), 1378.

$C_9H_{17}ON_2$ Phenylmethylethylazonium hydroxides, salts of, and their resolution (SINGH), 1204.

$C_9H_{22}NI$ Triethyl-α-propylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1314.

9 IV

$C_9HO_4NBr_4$ Tetrabromo-6-nitrocoumarin (DHAR), 1000.

$C_9H_2O_4NBr_3$ Tribromo-6-nitrocoumarin (DHAR), 1000.

$C_9H_3O_4NBr_2$ 3:8-Dibromo-6-nitrocoumarin (DHAR), 1000.

$C_9H_3O_6N_2Br$ 3-Bromo-6:8-dinitrocoumarin (DHAR), 1000.

$C_9H_6O_2NBr$ 5-Bromoveratronitrile (WENTWORTH and BRADY), 1045.

$C_9H_{10}O_2NBr$ 5-Bromo-3:4-dimethoxybenzaldoximes (WENTWORTH and BRADY), 1044.

$C_9H_{10}O_7N_2S$ Dinitro-ψ-cumene-5-sulphonic acid ($+4H_2O$), and its salts (GIBSON), 953.

Dinitromesitylenesulphonic acid ($+4H_2O$), and its salts (GIBSON), 950.

$C_9H_{11}O_6N_3S$ Dinitro-ψ-cumene-5-sulphonamide (GIBSON), 955.

Dinitromesitylenesulphonamide (GIBSON), 951.

$C_9H_{12}O_5N_2S$ Nitroamino-ψ-cumene-5-sulphonic acid (GIBSON), 956.

$C_9H_{14}O_3N_2S$ Diamino-ψ-cumene-5-sulphonic acid (GIBSON), 956.

Diaminomesitylenesulphonic acid (GIBSON), 952.

$C_9H_{23}O_4N_4Co$ *cis*-Dimethylmalonatodiethylenediaminecobaltic hydroxide, salts of (PRICE and DUFF), 1076.

9 V

$C_9H_9O_6N_2ClS$ Dinitro-ψ-cumene-5-sulphonyl chloride (GIBSON), 955.

Dinitromesitylenesulphonyl chloride (GIBSON), 950.

$C_9H_{11}O_2N_2ClS$ Thiocarbamide benzyl chloroacetate (TAYLOR), 8.

$C_9H_{22}O_4N_4ClCo$ *cis*-Dimethylmalonatodiethylenediaminecobaltic chloride (PRICE and DUFF), 1077.

$C_9H_{22}O_4N_4BrCo$ *cis*-Dimethylmalonatodiethylenediaminecobaltic bromide ($+2H_2O$) (PRICE and DUFF), 1077.

C_{10} Group.

$C_{10}H_{16}$ *d*-Carene (SIMONSEN), 574.

1-Methyl-3-*iso*propyl-$\Delta^{4:6}$-*cyclo*hexadiene (HENDERSON and SMEATON), 149.

$C_{10}H_{18}$ 1-Methyl-3-*iso*propyl-Δ^{5}-*cyclo*hexene (HENDERSON and SMEATON), 148.

10 II

$C_{10}H_2Br_6$ Hexabromonaphthalene (DHAR), 997.

$C_{10}H_4Br_4$ Tetrabromonaphthalenes (DHAR), 997.

$C_{10}H_6O_6$ 4-Hydroxy-3:5-dimethoxyphthalic anhydride (ALIMCHANDANI and MELDRUM), 970.

$C_{10}H_{10}O_2$ α-Benzylacrylic acid (SIMONSEN), 567.

$C_{10}H_{10}O_5$ 4-Hydroxy-3:5-dimethoxyphthalide (ALIMCHANDANI and MELDRUM), 969.

$C_{10}H_{10}O_7$ 4-Hydroxy-3:5-dimethoxyphthalic acid (ALIMCHANDANI and MELDRUM), 970.

$C_{10}H_{10}O_7$ 3:4:5-Trimethoxyphthalide, preparation of (ALIMCHANDANI and MELDRUM), 969.
$C_{10}H_{10}N_4$ *o*- and *p*-Tolueneazoglyoxalines (PYMAN and RAVALD), 1426.
$C_{10}H_{11}N$ Dihydro-α-naphthylamines, and their hydrochlorides (ROWE and LEVIN), 1576.
$C_{10}H_{12}O_5$ 3:4:5-Trimethoxybenzoic acid, salts of (ALIMCHANDANI and MELDRUM), 967.
$C_{10}H_{12}O_6$ ββ-Dihydroxydimethylpropanecarbethoxydicarboxylic acid dilactone (BEESLEY and THORPE), 611.
$C_{10}H_{12}N_4$ 2:4′-Diamino-4-*m*-tolylglyoxaline, and its salts (PYMAN and RAVALD), 1428.
$C_{10}H_{13}Br$ 4-Bromo-*n*-butylbenzene (REILLY and HICKINBOTTOM), 112.
$C_{10}H_{14}O$ *p-sec.*-Butylphenol, preparation of (REILLY and HICKINBOTTOM), 122.
4-Hydroxy-*n*-butylbenzene (REILLY and HICKINBOTTOM), 114.
6-Hydroxy-*m*-*iso*cymene (HENDERSON and SMEATON), 147.
$C_{10}H_{14}O_2$ 2:4-Dimethoxyethylbenzene (NIERENSTEIN), 973.
$C_{10}H_{15}N$ Amino-*n*- and *-sec.*-butylbenzenes, and their salts (REILLY and HICKINBOTTOM), 110, 126.
n- and *sec.*-Butylanilines, and their salts (REILLY and HICKINBOTTOM), 121, 126.
$C_{10}H_{13}As$ Phenyldiethylarsine, preparation of (BURROWS and TURNER), 1379.
$C_{10}H_{16}N_2$ 4-*n*-Butyl-*o*-phenylenediamine (REILLY and HICKINBOTTOM), 118.
$C_{10}H_{18}O$ *iso*Pulegol, physical properties of, and of its esters (PICKARD, HUNTER, LEWCOCK, and PENNINGTON), 1248.
$C_{10}H_{18}O_2$ *d*-Careneglycol (SIMONSEN), 576.
$C_{10}H_{18}O_4$ *l*-Hexylsuccinic acid (WREN and BURNS), 266.
$C_{10}H_{18}Br_2$ 5:6-Dibromo-1-methyl-3-*iso*propyl*cyclo*hexane (HENDERSON and SMEATON), 148.
$C_{10}H_{20}O$ 1-Methyl-3-*iso*propyl*cyclo*hexan-6-ol (HENDERSON and SMEATON), 147.
$C_{10}H_{20}O_6$ Tetramethyl fructoses (HAWORTH), 207; (IRVINE and STEELE), 1488.

10 III

$C_{10}H_9O_3N_3$ 3-Cyano-2:6-diketo-4-propylpiperidine-5-carboxylamide (DAY and THORPE), 1472.
$C_{10}H_4O_8N_2$ 1:2:6:8-Tetranitronaphthalene (DHAR), 1004.
$C_{10}H_7ONa$ Sodium β-naphthoxide, action of alkyl iodides with (COX), 493.
$C_{10}H_9ON$ 1-Methyl-2-quinolone, preparation of (MILLS and WISHART), 585.
$C_{10}H_{10}O_2Br_2$ αβ′-Dibromo-β-phenyl*iso*butyric acid (SIMONSEN), 568.
$C_{10}H_{11}ON_3$ 2-*p*-Aminophenyl-5-methyl-4-glyoxalone, and its hydrochloride (FARGHER), 679.
$C_{10}H_{11}O_2Br$ Bromo-β-phenyl*iso*butyric acids (SIMONSEN), 568.
$C_{10}H_{11}O_8N_5$ Trinitrophenyl-*n*-butylnitroamine (REILLY and HICKINBOTTOM), 135.
$C_{10}H_{12}O_4Se_2$ Selenium acetylacetone (MORGAN and DREW), 1456.
$C_{10}H_{12}O_8N_6$ Substance, from the action of ammonia on tetryl (JAMES, JONES, and LEWIS), 1275.
$C_{10}H_{13}O_2N$ β′-Amino-β-phenyl*iso*butyric acid (SIMONSEN), 569.
Nitro-*n*-butylbenzenes (REILLY and HICKINBOTTOM), 116.
$C_{10}H_{13}O_3N$ Nitro-*p-sec.*-butylphenol (REILLY and HICKINBOTTOM), 123.
$C_{10}H_{14}ON_2$ Benzyldimethylcarbamide (WERNER), 1051.
Phenyl-*sec.*-butylnitrosoamine (REILLY and HICKINBOTTOM), 121.

$C_{10}H_{14}O_2N_2$ Nitroamino-*n*-butylbenzenes, and their salts (REILLY and HICKINBOTTOM), 115.

$C_{10}H_{14}O_2N_4$ $\alpha\alpha'$-Dicyano-β-propylglutaramide (DAY and THORPE), 1471.

6-Imino-3-cyano-5-carbamyl-4-propyl-2-piperidone (DAY and THORPE), 1472.

$C_{10}H_{14}N_2S$ Benzyldimethylthiocarbamide (WERNER), 1051.

$C_{10}H_{16}O_2N_2$ Dimethylammonium benzylcarbamate (WERNER), 1051.

$C_{10}H_{16}O_3N_2$ *d*-Carene nitrosate (SIMONSEN), 574.

$C_{10}H_{16}NI$ Phenyldimethylethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1316.

$C_{10}H_{16}N_2S_2$ Dimethylammonium benzyldithiocarbamate (WERNER), 1051.

$C_{10}H_{16}IAS$ Phenylmethylethylarsine methiodide (BURROWS and TURNER), 1381.

$C_{10}H_{16}I_2As_2$ Substance, from phenyldimethylarsine and ethyldi-iodoarsine (BURROWS and TURNER), 1379.

Substance, from phenylmethylethylarsine and methyldi-iodoarsine (BURROWS and TURNER), 1381.

$C_{10}H_{17}N_2I$ *dl*-Phenylmethylpropylazonium iodide (SINGH), 1211.

$C_{10}H_{18}O_4S$ Methyl γ-thiodibutyrate (DAVIES), 304.

$C_{10}H_{19}O_3N_3$ Triacetyl derivative of diethylenetriamine (FARGHER), 1354.

$C_{10}H_{24}NI$ Methyltri-α-propylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1315.

10 IV

$C_{10}H_3ONBr_4$ Tetrabromonitronaphthalenes (DHAR), 997.

$C_{10}H_8O_3N_2S$ Carbophenoxy*iso*thiohydantoin (DIXON and KENNEDY), 79.

$C_{10}H_{10}ON_3Br$ 2-Methyl-4-(2′-amino-5′-bromophenyl)-5-glyoxalone (+ H_2O), and its salts (FARGHER), 677.

$C_{10}H_{10}O_3NBr$ Acetyl derivative of 5-bromo-*o*-methoxybenzaldoxime (WENTWORTH and BRADY), 1044.

10 V

$C_{10}H_{11}O_2N_2Cl_3S$ Thiocarbamide benzyl trichloroacetate (TAYLOR), 10.

$C_{10}H_{12}O_2N_2Cl_2S$ Thiocarbamide benzyl dichloroacetate (TAYLOR), 10.

C_{11} Group.

$C_{11}H_{10}O_7$ 4-Hydroxy-3:5-dimethoxyphthalide-2-carboxylic acid (+ H_2O), and its calcium salt (ALIMCHANDANI and MELDRUM), 968.

$C_{11}H_{11}N_3$ 4-Benzylideneamino-5-methylglyoxaline (FARGHER), 676.

$C_{11}H_{12}O_7$ 3:4:5-Trimethoxyphthalic acid, preparation of (ALIMCHANDANI and MELDRUM), 969.

$C_{11}H_{14}O_2$ Ethyl *l*-α-hydroxy-β-phenylpropionate, hydrolysis of (MCKENZIE and WREN), 689.

$C_{11}H_{14}O_3$ β-Phenyl-α-methoxymethylpropionic acid, and its silver salt (SIMONSEN), 567.

$C_{11}H_{16}O_2$ Homocamphorquinone (LAPWORTH and ROYLE), 749.

$C_{11}H_{16}O_3$ *cyclo*Heptane-1:1-diacetic anhydride (DAY, KON, and STEVENSON), 645.

$C_{11}H_{16}O_5$ α-Ketohomocamphoric acid, and its salts (CHORLEY and LAPWORTH), 739.

$C_{11}H_{17}N$ Amino-*n*-butyltoluenes (REILLY and HICKINBOTTOM), 133.

4-Methylamino-*n*-butylbenzene (REILLY and HICKINBOTTOM), 131.

Methyl-*n*-butylaniline, and its salts (REILLY and HICKINBOTTOM), 130.

$C_{11}H_{18}O$ Homocamphor (LAPWORTH and ROYLE), 743.

$C_{11}H_{18}O_4$ *cyclo*Heptane-1:1-diacetic acid, and its silver salt (DAY, KON. and STEVENSON), 639.
Homocamphoric acid (LAPWORTH and ROYLE), 750.
$C_{11}H_{22}O_6$ Tetramethyl γ-methylfructoside (IRVINE and STEELE), 1486.

11 III

$C_{11}H_5O_8N_3$ Trinitro-β-naphthoic acid (DHAR), 1004.
$C_{11}H_9O_2N$ Cinchonic acid methylbetaine (MILLS and WISHART), 586.
$C_{11}H_9O_5Cl_3$ 4-Hydroxy-3:5-dimethoxy-2-trichloromethylphthalide (ALIMCHANDANI and MELDRUM), 968.
$C_{11}H_{14}O_6N_4$ Dinitro-*n*-butylphenyl-4-methylnitroamine (REILLY and HICKINBOTTOM), 132.
$C_{11}H_{15}ON_3$ Camphorquinonecyanohydrazone (FORSTER and SAVILLE), 756.
$C_{11}H_{15}O_2N$ *n*-Butyl phenylcarbamate (CHATTAWAY and SAERENS), 710.
$C_{11}H_{15}O_4Br$ Lactone of ethyl α-bromo-α-hydroxy*cyclo*pentane-1:1-diacetate (BECKER and THORPE), 1585.
$C_{11}H_{16}ON_2$ 4-*n*-Butylphenylmethylnitrosoamine (REILLY and HICKINBOTTOM), 132.
p-Nitrosomethyl-*n*-butylaniline (REILLY and HICKINBOTTOM), 131.
$C_{11}H_{17}O_2N$ Imide of *cyclo*heptane-1:1-diacetic acid (DAY, KON, and STEVENSON), 645.
*iso*Nitrosohomocamphor (LAPWORTH and ROYLE), 749.
$C_{11}H_{17}O_3N$ α-Camphidonecarboxylic acid, and its silver salt (CHORLEY and LAPWORTH), 741.
$C_{11}H_{17}O_4N$ Acid, and its isomeride, from nitrous acid and camphoroxalic acid (CHORLEY and LAPWORTH), 729.
$C_{11}H_{17}O_4Br$ Ethyl hydrogen α-bromo*cyclo*pentane-1:1-diacetic acid (BECKER and THORPE), 1586.
$C_{11}H_{17}O_5N$ α-*iso*Nitrosohomocamphoric acid (CHORLEY and LAPWORTH), 740.
$C_{11}H_{17}N_2Cl$ *dl*-Phenylethylallylazonium chloride, platinichloride of (SINGH), 1212.
$C_{11}H_{17}N_2I$ *dl*-Phenylethylallylazonium iodide (SINGH), 1212.
$C_{11}H_{18}NI$ Phenyldimethyl-α-propylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1317.
Phenylmethyldiethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1317.
$C_{11}H_{18}I_2As_2$ Substance, from phenyldiethylarsine and methyldi-iodoarsine (BURROWS and TURNER), 1380.
$C_{11}H_{19}ON$ Homocamphoroxime (LAPWORTH and ROYLE), 748.
$C_{11}H_{24}NI$ Ethyltri-α-propylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1315.

11 IV

$C_{11}H_9O_4NBr_2$ Diacetyl derivatives of dibromohydroxybenzaldoximes (WENTWORTH and BRADY), 1042.
$C_{11}H_{10}O_2NI$ Cinchonic acid methiodide (MILLS and WISHART), 586.
$C_{11}H_{10}O_3N_2S$ Phenylcarbomethoxy*iso*thiohydantoin (DIXON and KENNEDY), 77.
$C_{11}H_{12}O_2NCl_3$ *n*-Butyl 2:4:6-trichlorophenylcarbamate (CHATTAWAY and SAERENS), 710.
$C_{11}H_{12}O_4NBr$ Acetyl derivatives of 5-bromo-3:4-dimethoxybenzaldoximes (WENTWORTH and BRADY), 1044.
$C_{11}H_{13}O_2NCl_2$ *n*-Butyl 2:4-dichlorophenylcarbamate (CHATTAWAY and SAERENS), 710.

$C_{11}H_{13}O_2NBr_2$ *n*-Butyl 2:4-dibromophenylcarbamate (CHATTAWAY and SAERENS), 710.

$C_{11}H_{14}O_2NCl$ *n*-Butyl chlorophenylcarbamates (CHATTAWAY and SAERENS), 710.

$C_{11}H_{14}O_2NBr$ *n*-Butyl bromophenylcarbamates (CHATTAWAY and SAERENS), 710.

$C_{11}H_{14}O_2NI$ *n*-Butyl *p*-iodophenylcarbamate (CHATTAWAY and SAERENS), 711.

$C_{11}H_{16}O_2N_4S_2$ Benzyl-ψ-thiourea *iso*thiohydantoate (TAYLOR), 9.

11 IV

$C_{11}H_{13}O_2NClBr$ *n*-Butyl 2-chloro-4-bromophenylcarbamate (CHATTAWAY and SAERENS), 710.

C_{12} Group.

$C_{12}H_{12}O_3$ 2-Hydroxydiphenylacetic acid (GREENWOOD and NIERENSTEIN), 1598.

$C_{12}H_{12}N_2$ Benzidine, condensation of benzil with (FERRISS and TURNER), 1143.

$C_{12}H_{13}As$ α-Naphthyldimethylarsine (BURROWS and TURNER), 1381.

$C_{12}H_{14}O$ 1-Phenyl*cyclo*hexan-3-one (BOYD, CLIFFORD, and PROBERT), 1389.

$C_{12}H_{14}O_5$ Benzylmethoxymethylmalonic acid, and its salts (SIMONSEN), 565.

$C_{12}H_{14}O_6$ Lactone of hydroxycarbethoxymethane-II$^{1:3}$-3-methyl*cyclo*propane-1-carbethoxy-2-carboxylic acid (BEESLEY and THORPE), 616.

$C_{12}H_{15}Br$ 3-Bromo-1-phenyl*cyclo*hexane (BOYD, CLIFFORD, and PROBERT), 1388.

$C_{12}H_{16}O$ 1-Phenyl*cyclo*hexan-3-ol, preparation of (BOYD, CLIFFORD, and PROBERT), 1387.

$C_{12}H_{16}O_4$ Camphoroxalic acid, action of nitrous acid on (CHORLEY and LAPWORTH), 728.

$C_{12}H_{19}N$ 4-Ethylamino-*n*-butylbenzene (REILLY and HICKINBOTTOM), 132.
Ethyl-*n*-butylaniline, and its picrate (REILLY and HICKINBOTTOM), 132.

$C_{12}H_{22}O_4$ Diethyl β-propylglutarate (DAY and THORPE), 1472.

$C_{12}H_{22}O_{11}$ Sucrose, structure of (HAWORTH), 199; (ARMSTRONG and HILDITCH), 1086; mechanism of the inversion of (JONES and LEWIS), 1120.

12 III

$C_{12}H_4O_6N_2$ 3:4-Dinitroacenaphthenequinone (ROWE and DAVIES), 1350.

$C_{12}H_5O_4N$ 3-Nitroacenaphthenequinone (ROWE and DAVIES), 1349.

$C_{12}H_6O_2N_2$ Acenaphthene-7:8-*iso*oxadiazole oxide (ROWE and DAVIES), 1348.

$C_{12}H_6ON_2$ Acenaphthene-2:3-*iso*oxadiazole (ROWE and DAVIES), 1348.

$C_{12}H_6O_3N_2$ Acenaphthene-2:3-*iso*oxadiazole oxides (ROWE and DAVIES), 1346.

$C_{12}H_9O_2Cl$ β-Naphthyl chloroacetate (CROMPTON and VANDERSTICHELE), 692.

$C_{12}H_{10}O_2N_2$ Acenaphthene-2:3-quinonedioxime (ROWE and DAVIES), 1347.

$C_{12}H_{10}ClAs$ Diphenylarsenious chloride (MORGAN and VINING), 777.

$C_{12}H_{10}BrAs$ Diphenylarsenious bromide, preparation of (POPE and TURNER), 1451.

$C_{12}H_{10}IAs$ Diphenylarsenious iodide (POPE and TURNER), 1452.

$C_{12}H_{11}OCl$ 5-Chloro-1-phenyl-Δ^4-*cyclo*hexen-3-one (BOYD, CLIFFORD, and PROBERT), 1386.

$C_{12}H_{11}O_2Br$ 4-Bromophenyldihydroresorcin (BOYD, CLIFFORD, and PROBERT), 1385.

$C_{12}H_{13}ON$ Dihydroaceto-α-naphthalides (Rowe and Levin), 1576.
$C_{12}H_{15}ON$ Oxime of 1-phenyl*cyclo*hexan-3-one (Boyd, Clifford, and Probert), 1389.
$C_{12}H_{16}O_3N_2$ 3-Nitro-4-acetylamino-*n*-butylbenzene (Reilly and Hickinbottom), 117.
$C_{12}H_{17}ON$ Acetylamino-*n*- and -*sec*.-butylbenzenes (Reilly and Hickinbottom), 111.
$C_{12}H_{17}ON_3$ Methyl derivative of camphorquinonecyanohydrazone (Forster and Saville), 756.
$C_{12}H_{17}O_2N$ *n*-Butyl tolylcarbamates (Chattaway and Saerens), 711.
$C_{12}H_{18}ON_2$ Benzyldiethylcarbamide (Werner), 1051.
4-*n*-Butylphenylethylnitrosoamine and *p*-Nitrosoethyl-*n*-butylaniline, and its zincichloride (Reilly and Hickinbottom), 132.
$C_{12}H_{18}N_2S$ Benzyldiethylthiocarbamide (Werner), 1052.
$C_{12}H_{19}O_2N_3$ Base, from camphorquinonecyanohydrazone, and sulphuric acid (Forster and Saville), 758.
Camphorquinonemethylsemicarbazone ($+\frac{1}{2}H_2O$) (Forster and Saville), 760.
$C_{12}H_{19}O_4N$ Methyl derivative of acid $C_{11}H_{17}O_4N$ (Chorley and Lapworth), 738.
$C_{12}H_{20}O_2N_2$ Diethylammonium benzylcarbamate (Werner), 1051.
$C_{12}H_{20}NI$ Phenyltriethylammonium iodide, mercuri-iodides of, and their crystallography (Barker and Porter), 1318.
$C_{12}H_{20}N_2S_2$ Diethylammonium benzyldithiocarbamate (Werner), 1052.
$C_{12}H_{21}ON_3$ Homocamphorsemicarbazone (Lapworth and Royle), 748.
$C_{12}H_{22}O_4S$ Ethyl γ-thiodibutyrate (Davies), 302.
$C_{12}H_{28}NI$ Tetra-α-propylammonium iodide, mercuri-iodide of, and its crystallography (Barker and Porter), 1316.

12 IV

$C_{12}H_{10}ON_2B$ Boryldiazoaminobenzene (Chaudhuri), 1084.
$C_{12}H_{12}ONCl$ Oxime of 5-chloro-1-phenyl-Δ^4-*cyclo*hexen-3-one (Boyd, Clifford, and Probert), 1386.
$C_{12}H_{12}ON_2B$ Boro-α-phenyl-β-aminophenylhydrazide (Chaudhuri), 1085.
Borylhydrazoaminobenzene (Chaudhuri), 1085.
$C_{12}H_{13}O_2N_2As_2$ 3:3′-Diamino-4:4′-dihydroxyarsenobenzene, dihydrochloride (salvarsan), preparation of (Fargher and Pyman), 370.
$C_{12}H_{12}O_3N_2S$ Phenylcarbethoxy*iso*thiohydantoin (Dixon and Kennedy), 76.

C_{13} Group.

$C_{13}H_8O_2$ Xanthone, formation, structure, and derivatives of (Dhar), 1053.
$C_{13}H_9N$ 4-Cyanodiphenyl, preparation of (Ferriss and Turner), 1148.
$C_{13}H_{10}O_3$ 2:4-Dihydroxybenzophenone, preparation of (Stephen), 1529.
$C_{13}H_{10}O_4$ 2:4:4′-Trihydroxybenzophenone, preparation of (Stephen), 1529.
$C_{13}H_{12}O_2$ Substance, from the resin of *Xanthorrhœa* (Rennie, Cooke, and Finlayson), 347.
$C_{13}H_{13}As$ Diphenylmethylarsine (Burrows and Turner), 1381.
$C_{13}H_{14}N_2$ Diaminodiphenylmethane, preparation of (King), 988.
$C_{13}O_2Br_8$ Octabromoxanthone (Dhar), 999.

13 III

$C_{13}H_2O_2Br_6$ Hexabromoxanthone (Dhar), 999.
$C_{13}H_4O_2Br_4$ Tetrabromoxanthone (Dhar), 999.

$C_{13}H_4O_{10}N_4$ Tetranitroxanthones (DHAR), 1065.
$C_{13}H_5O_9N_3$ Trinitroxanthones (DHAR), 1064.
$C_{13}H_6O_2Cl_2$ Dichloroxanthone (DHAR), 1069.
$C_{13}H_6O_6N_2$ Dinitroxanthones (DHAR), 1063.
$C_{13}H_7O_2Cl$ Chloroxanthones (DHAR), 1067.
$C_{13}H_7O_3Br$ Bromoxanthones (DHAR), 1069.
$C_{13}H_7O_4N$ Nitroxanthones (DHAR), 1061.
$C_{13}H_7O_6N_3$ Dinitromonoaminoxanthone (DHAR), 1064.
$C_{13}H_8O_8N_2$ Dinitroxanthhydrols (DHAR), 1067.
$C_{13}H_{10}O_6N_4$ 2:4:6-Trinitrophenylbenzylamine (JAMES, JONES, and LEWIS), 1275.
$C_{13}H_{10}NAs$ Diphenylarsenious cyanide (MORGAN and VINING), 777.
Diphenylcyanoarsine (MCKENZIE and WOOD), 411.
$C_{13}H_{11}O_5N_3$ Azo-colouring matter from 3:5-dinitro-*o*-toluidine and resorcinol (MORGAN and DREW), 791.
$C_{13}H_{11}O_6Cl_3$ 4-Acetoxy-3:5-dimethoxy-2-trichloromethylphthalide (ALIMCHANDANI and MELDRUM), 968.
$C_{13}H_{12}ON_4$ 4:4′-Diamino-2:2′-azoxydiphenylmethane, and its dihydrochloride (KING), 992.
$C_{13}H_{12}O_4N_4$ 3′:4-Dinitro-2:4′-diaminodiphenylmethane (KING), 990.
$C_{13}H_{13}O_8N_6$ Substance, from aniline and tetryl (JAMES, JONES, and LEWIS), 1275.
$C_{13}H_{13}O_2N_3$ 4-Nitro-2:4′-diaminodiphenylmethane, and its dihydrochloride (KING), 989.
$C_{13}H_{13}O_6N_7$ Substance, from *m*-phenylenediamine and tetryl (JAMES, JONES, and LEWIS), 1278.
$C_{13}H_{15}O_3N_3$ ω-Imide of $\alpha\alpha_1$-dicyano*cyclo*heptane-1:1-diacetic acid (DAY, KON, and STEVENSON), 643.
$C_{13}H_{16}IAs$ α-Naphthyldimethylarsine methiodide (BURROWS and TURNER), 1381.
$C_{13}H_{16}I_2As_2$ Substance, from α-naphthyldimethylarsine and methyldi-iodoarsine (BURROWS and TURNER), 1382.
$C_{13}H_{17}ON_3$ Semicarbazone of 1-phenyl*cyclo*hexan-3-one (BOYD, CLIFFORD, and PROBERT), 1389.
$C_{13}H_{17}O_3N_3$ Acetyl derivative of camphorquinonecyanohydrazone (FORSTER and SAVILLE), 757.
$C_{13}H_{19}ON$ Acetylamino-*n*-butyltoluenes (REILLY and HICKINBOTTOM), 133.
$C_{13}H_{19}O_4N_3$ ω-Imide of $\alpha\alpha_1$-dicarbamyl*cyclo*heptane-1:1-diacetic acid (DAY, KON, and STEVENSON), 644.
$C_{13}H_{20}O_4Br_2$ Ethyl $\alpha\alpha'$-dibromo*cyclo*pentane-1:1-diacetate (BECKER and THORPE), 1585.
$C_{13}H_{21}O_2N_3$ Base, from camphorquinonecyanohydrazone and hydrochloric acid (FORSTER and SAVILLE), 757.
$C_{13}H_{21}O_4N$ Dimethyl derivative of acid $C_{11}H_{17}O_4N$ (CHORLEY and LAPWORTH), 738.
$C_{13}H_{21}O_4Br$ Ethyl $\alpha\alpha'$-bromo*cyclo*pentane-1:1-diacetate (BECKER and THORPE), 1586.
$C_{13}H_{22}NI$ Phenyldiethyl-α-propylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1319.

13 IV

$C_{13}H_3O_{10}N_4Cl$ Chlorotetranitroxanthones (DHAR), 1068.
$C_{13}H_3O_{10}N_4Br$ Bromotetranitroxanthones (DHAR), 1070.
$C_{13}H_4O_6N_2Cl_2$ Dichlorodinitroxanthone (DHAR), 1069.
$C_{13}H_4O_6N_2Br_2$ Dibromodinitroxanthone (DHAR), 998.

$C_{13}H_4O_8N_3Cl$ Chlorotrinitroxanthone (DHAR), 1068.
$C_{13}H_5O_6N_2Cl$ Chlorodinitroxanthone (DHAR), 1069.
$C_{13}H_5O_6N_2Br$ Bromodinitroxanthone (DHAR), 1070.
$C_{13}H_7O_5Cl_3Sn$ Substance, from stannic chloride and 2:3:8-trihydroxyxanthone (DEAN and NIERENSTEIN), 805.
$C_{13}H_8O_4N_2Cl_2$ 4:4′-Dichloro-3:3′-dinitrodiphenylmethane (STEPHEN, SHORT, and GLADDING), 523.
$C_{13}H_{10}O_2NB$ Benzoylboranilide (CHAUDHURI), 1082.
$C_{13}H_{10}NCl_2As$ Diphenylcyanoarsine dichloride (MCKENZIE and WOOD), 415.
$C_{13}H_{11}ON_2As_2$ 3′-Amino-4′-hydroxy-1:3-diazole-5:1′-arsenobenzene, and its hydrochloride (FARGHER), 875.
$C_{13}H_{14}ON_2Cl$ Semicarbazone of 5-chloro-1-phenyl-Δ^4-*cyclo*hexen-3-one (BOYD, CLIFFORD, and PROBERT), 1386.

13 V

$C_{13}H_9O_2NBrB$ Benzoyl-*p*-bromoboranilide (CHAUDHURI), 1084.

C_{14} Group.

$C_{14}H_8N_2$ 4:4′-Dicyanodiphenyl, preparation of (FERRISS and TURNER), 1149.
$C_{14}H_{10}O_2$ Benzil, condensation of benzidine with (FERRISS and TURNER), 1143.
$C_{14}H_{10}O_5$ 2:3-Dihydroxy-8-methoxyxanthone, preparation of (DEAN and NIERENSTEIN), 803.
$C_{14}H_{12}O$ 4-Phenylacetophenone, preparation of (FERRISS and TURNER), 1147.
$C_{14}H_{18}O_2$ Acetyl derivative of 1-phenyl*cyclo*hexan-3-ol (BOYD, CLIFFORD, and PROBERT), 1388.
$C_{14}H_{16}O_6$ Ethyl methylmethane-III$^{1:2:3}$-*cyclo*propane-1:2:3-tricarboxylate (BEESLEY and THORPE), 617.
$C_{14}H_{22}O_4$ Bornyl hydrogen tartrates, and their salts (WREN, WILLIAMS, and MYDDLETON), 194.
$C_{14}H_{23}N$ 4-Amino-1:3-di-*n*-butylbenzene (REILLY and HICKINBOTTOM), 123.
$C_{14}H_{24}O_4$ Dimethyl hydrocamphorylacetate (LAPWORTH and ROYLE), 747.

14 III

$C_{14}H_6O_2Br_2$ 1:3-Dibromoanthraquinone (DHAR), 1002.
$C_{14}H_6O_6N_2$ 1:3-Dinitroanthraquinone (DHAR), 1003.
$C_{14}H_7O_4N_3$ 3-Nitro-1-aminoanthraquinone (DHAR), 1003.
$C_{14}H_{12}O_4N_4$ Dinitroazotoluene (KENNER and PARKIN), 857.
$C_{14}H_{12}O_6N_4$ 2:4:6-Trinitrophenyl-*m*-xylylamine (JAMES, JONES, and LEWIS), 1277.
$C_{14}H_{14}O_3N_2$ Phloroacetophenonephenylhydrazone (SEN and GHOSH), 63.
$C_{14}H_{14}O_4As_2$ Dihydroxydimethoxyarsenobenzenes (FARGHER), 872.
$C_{14}H_{14}O_6N_6$ Substance, from methylaniline and tetryl (JAMES, JONES, and LEWIS), 1278.
Substance, from *o*- and *p*-toluidines and tetryl (JAMES, JONES, and LEWIS), 1276.
$C_{14}H_{15}O_6As$ 4:4′-Dihydroxy-3:3′-dimethoxydiphenylarsinic acid (FARGHER), 873.
$C_{14}H_{13}Cl_2As_2$ Substance, from phenyldimethylarsine and phenyldichloroarsine (BURROWS and TURNER), 1379.
$C_{14}H_{13}I_2As_2$ Substance, from phenyldimethylarsine and phenyldi-iodoarsine (BURROWS and TURNER), 1379.
$C_{14}H_{19}O_3N$ β-Propylglutaric semianilide (DAY and THORPE), 1472.
$C_{14}H_{15}O_6Br$ Ethyl bromocarbethoxymethane-II$^{1:3}$-3-methyl*cyclo*propane-1:2-dicarboxylates (BEESLEY and THORPE), 615.

$C_{14}H_{21}O_6Br_3$ Ethyl $\alpha\beta\beta$-tribromodimethylpropanetricarboxylate (BEESLEY and THORPE), 619.

$C_{14}H_{22}ON_2$ 4-*n*-Butylphenyl-*n*-butylnitrosoamine (REILLY and HICKINBOTTOM), 124.

$C_{14}H_{21}O_6Br_2$ Ethyl $\beta\beta$-dibromodimethylpropanetricarboxylate (BEESLEY and THORPE), 610.

14 IV

$C_{14}H_9O_2N_2Br$ α- and β-Phthalyl-*p*-bromophenylhydrazides (CHATTAWAY and TESH), 715.

$C_{14}H_{12}O_4N_2S$ Dinitroditolyl sulphide (KENNER and PARKIN), 857.

$C_{14}H_{12}O_8N_2As_2$ 5:5′-Dinitrodihydroxydimethoxyarsenobenzenes (FARGHER), 873.

$C_{14}H_{15}O_3N_3S$ Methyl-orange, effect of temperature on the colour changes of (TIZARD and WHISTON), 150.

$C_{14}H_{16}O_4N_2As_2$ Diaminodihydroxydimethoxyarsenobenzenes, and their hydrochlorides (FARGHER), 873.

C_{15} Group.

$C_{15}H_{24}$ *d*-Longifolene, and its salts (SIMONSEN), 578.

15 II

$C_{15}H_8O_5$ 8-Hydroxy-2:3-quinoxanthone, preparation of (DEAN and NIERENSTEIN), 802.

$C_{15}H_8O_4$ Anthraquinone-1-carboxylic acid, preparation of (PERKIN), 706.

$C_{15}H_{10}O_5$ 2:3-Methylenedioxy-8-methoxyxanthone, preparation of (DEAN and NIERENSTEIN), 803.

$C_{15}H_{12}O_2$ 3-Phenyldihydrocoumarin, preparation of (GREENWOOD and NIERENSTEIN), 1596.

$C_{15}H_{12}O_5$ 8-Hydroxy-2:3-dimethoxyxanthone (DEAN and NIERENSTEIN), 805.

$C_{15}H_{12}O_6$ Colouring matter ($+ 2H_2O$) from *Hyenanche globosa* (HENRY), 1625.

$C_{15}H_{14}O$ 3-Phenylchroman (GREENWOOD and NIERENSTEIN), 1597.

$C_{15}H_{14}O_6$ Catechin, constitution of (NIERENSTEIN), 971, 1151.

$C_{15}H_{16}O$ 2-Hydroxy-$\alpha\alpha$- and -$\alpha\gamma$-diphenylpropanes (GREENWOOD and NIERENSTEIN), 1595.

$C_{15}H_{16}O_2$ 2:ω-Dihydroxy-$\alpha\alpha$-diphenylpropane (GREENWOOD and NIERENSTEIN), 1596.

$C_{15}H_{17}As$ Di-*o*-tolylmethylarsine (BURROWS and TURNER), 1383.

$C_{15}H_{10}O_7$ *n*- and *iso*-Hyenanchin (HENRY), 1619.

15 III

$C_{15}H_8O_9N_2$ 5:5′-Dinitrobenzophenone-2:2′-dicarboxylic acid (STEPHEN, SHORT, and GLADDING), 527.

$C_{15}H_{10}O_3N_2$ α-Phthalylformylphenylhydrazide (CHATTAWAY and TESH), 717.

$C_{15}H_{12}O_2N_2$ α- and β-Phthalyltolylhydrazides (CHATTAWAY and TESH), 716.

$C_{15}H_{13}O_3N_3$ *p*-Nitrophenylhydrazones of methylcoumaranones (HIGGINBOTHAM and STEPHEN), 1541.

$C_{15}H_{15}ON$ 4-Acetylaminodiphenylmethane (KING), 990.

$C_{15}H_{15}O_2N$ Tolyloxyacetanilides (HIGGINBOTHAM and STEPHEN), 1540.

$C_{15}H_{15}O_5N_3$ ω-Methoxyresacetophenone *p*-nitrophenylhydrazone (SLATER and STEPHEN), 313.

$C_{15}H_{17}O_3N$ Anilic acid of *cis-cyclo*pentane*spirocyclo*propane-1:2-dicarboxylic acid (BECKER and THORPE), 1588.

$C_{15}H_{16}NI$ Phenylbenzyldimethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1319.

$C_{15}H_{18}IAs$ Phenyldimethylarsine benziodide (BURROWS and TURNER), 1378.

$C_{15}H_{15}I_3As_2$ Substance, from phenylmethylethylarsine and phenyldi-iodoarsine (BURROWS and TURNER), 1381.

15 IV

$C_{15}H_9O_3N_2Br$ α-Phthalylformyl-*p*-bromophenylhydrazide (CHATTAWAY and TESH), 717.

$C_{15}H_{11}O_5Cl_3Sn$ Substance, from stannic chloride and 8-hydroxy-2:3-dimethoxyxanthone (DEAN and NIERENSTEIN), 805.

C_{16} Group.

$C_{16}H_{12}O_6$ 5:7:2′:4′:6′-Pentahydroxy-2-phenyl-4-methylene-1:4-benzopyran (SEN and GHOSH), 62.

$C_{16}H_{14}O_2$ 4:4′-Diacetyldiphenyl, and its condensations with aromatic amines (FERRISS and TURNER), 1140.

$C_{16}H_{16}O$ 2-Hydroxy-αα- and -αγ-diphenylpropane methyl ethers (GREENWOOD and NIERENSTEIN), 1595.

$C_{16}H_{20}N_2$ Camphanodihydroquinoxaline (B. K. and D. SINGH, DUTT, and G. SINGH), 986.

$C_{16}H_{22}O_5$ Ethyl benzylmethoxymethylmalonate (SIMONSEN), 566.

$C_{16}H_{30}O_{11}$ Anhydro-acid from tetramethyl fructose (HAWORTH), 208.

16 III

$C_{16}H_8O_4N_2$ Nitroxanthoquinoline (DHAR), 1066.

$C_{16}H_{12}O_2N_2$ α- and β-Phthalylacetylphenylhydrazides (CHATTAWAY and TESH), 717.

α-Phthalylformyltolylhydrazides (CHATTAWAY and TESH), 718.

$C_{16}H_{12}O_4N_2$ 2:4-Dinitrophenyldihydro-α-naphthylamines (ROWE and LEVIN), 1577.

$C_{16}H_{14}O_2N_2$ α- and β-Phthalylphenylethylhydrazides (CHATTAWAY and TESH), 712.

$C_{16}H_{16}O_2N_4$ Ethylidenebisphenylcarbamide (FARGHER), 679.

$C_{16}H_{18}O_3N_2$ 2:2′-Dimethoxy-3-3′-azoxytoluene (KENNER and PARKIN), 856.

$C_{16}H_{18}O_4As_2$ 3:4:3′:4′-Tetramethoxyarsenobenzene (FARGHER), 870.

$C_{16}H_{19}O_2N$ *iso*Nitrosocamphor *N*-phenyl ether (FORSTER and SAVILLE), 761.

$C_{16}H_{19}N_2I$ *dl*-Phenylbenzylallylazonium iodide (SINGH), 1212.

$C_{16}H_{20}ON_2$ Phenylbenzylallylazonium hydroxide, salts of, and their resolution (SINGH), 1213.

$C_{16}H_{20}NI$ Phenylbenzylmethylethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1320.

$C_{16}H_{20}IAs$ Di-*o*-tolylmethylarsine methiodide (BURROWS and TURNER), 1383.

$C_{16}H_{21}N_2Cl$ Phenylbenzylpropylazonium chloride, and its salts (SINGH), 1207.

$C_{16}H_{21}N_2I$ Phenylbenzylpropylazonium iodide (SINGH), 1207.

$C_{16}H_{22}ON_2$ Phenylbenzylpropylazonium hydroxide, salts of, and their resolution (SINGH), 1208.

16 IV

$C_{16}H_4O_3N_2Br$ α-Phthalylacetyl-*p*-bromophenylhydrazide (CHATTAWAY and TESH), 717.

$C_{16}H_{20}ONBr$ Bromophenylaminocamphor, optical rotation of (B. K. and D. Singh, Dutt, and G. Singh), 983.

$C_{16}H_{20}O_4N_2As_2$ Substance, from reduction of 5-amino-3:4-dimethoxyphenylarsinic acid (Fargher), 872.

C_{17} Group.

$C_{17}H_8O_8$ Ketodilactone of benzophenone-2:4:2′:4′-tetracarboxylic acid, and its resolution (Mills and Nodder), 1407.

$C_{17}H_{10}O$ Benzanthrone, properties of, and its salts (Perkin), 696.

$C_{17}H_{10}O_2$ Hydroxybenzanthrone, and its sulphate (Perkin), 698.

$C_{17}H_{10}O_3$ Benzalizarin, and its salts (Perkin), 702.

$C_{17}H_{14}O_6$ 8-Acetoxy-2:3-dimethoxyxanthone (Dean and Nierenstein), 805.

$C_{17}H_{15}N$ Benzylidenedihydro-α-naphthylamines (Rowe and Lewis), 1576.

$C_{17}H_{16}O_4$ Euxanthone diethyl ether, salts of (Perkin), 699.

$C_{17}H_{17}N$ Benzylidene-*ar*-tetrahydro-α-naphthylamine (Rowe and Levin), 1579.

$C_{17}H_{18}O_2$ Benzoyl derivative of *p-sec.*-butylphenol (Reilly and Hickinbottom), 123.

17 III

$C_{17}H_{12}O_5N_4$ 3:5-Dinitrotoluene-2-azo-β-naphthol (Morgan and Drew), 791.

$C_{17}H_{14}O_2N_2$ α- and β-Phthalylphenylallylhydrazides (Chattaway and Tesh), 714.

$C_{17}H_{14}O_3N_2$ α-Phthalylacetyltolylhydrazides (Chattaway and Tesh), 718.

α-Phthalylpropionylphenylhydrazide (Chattaway and Tesh), 717.

$C_{17}H_{14}O_8N_6$ Substance, from naphthylamines and tetryl (James, Jones, and Lewis), 1277.

$C_{17}H_{15}ON_3$ 2-*p*-Benzylideneaminophenyl-5-methyl-4-glyoxalone, and its acetate (Fargher), 679.

$C_{17}H_{16}O_2N_2$ α- and β-Phthalylphenylpropylhydrazides (Chattaway and Tesh), 713.

$C_{17}H_{16}O_6N_4$ 4:3′-Dinitro-2:4′-diacetylaminodiphenylmethane (King), 990.

$C_{17}H_{17}O_4N_3$ Diacetyl derivative of 4-nitro-2:4′-diaminodiphenylmethane (King), 989.

$C_{17}H_{19}ON$ Benzoylamino-*n*-butylbenzenes (Reilly and Hickinbottom), 111.

$C_{17}H_{19}O_2N$ 4-*n*-Butylphenyl phenylcarbamate (Reilly and Hickinbottom), 115.

$C_{17}H_{20}ON_2$ α-Phenyl-β-4-*n*- and *sec.*-butylphenylcarbamides (Reilly and Hickinbottom), 112, 120.

$C_{17}H_{22}O_4N_2$ Phenylhydrazone ($+H_2O$) of α-ketohomocamphoric acid (Chorley and Lapworth), 740.

$C_{17}H_{22}NI$ Phenylbenzyldiethylammonium iodide, mercuri-iodide of, and its crystallography (Barker and Porter), 1320.

Phenylbenzylmethyl-α-propylammonium iodide, mercuri-iodide of, and its crystallography (Barker and Porter), 1321.

$C_{17}H_{23}ON$ Tolylaminocamphor, optical rotation of (B. K. and D. Singh, Dutt, and G. Singh), 982.

$C_{17}H_{23}O_2N$ *o*-Methoxyphenylaminocamphor (B. K. and D. Singh, Dutt, and G. Singh), 985.

$C_{17}H_{23}O_3N$ *cyclo*Heptane-1:1-diacetic acid semianilide (Day, Kon, and Stevenson), 645.

$C_{17}H_{24}ON_2$ Substance, from suberone, ethyl cyanoacetate and ammonia (DAY, KON, and STEVENSON), 646.

17 IV

$C_{17}H_{13}O_2N_2Br$ α- and β-Phthalyl-*p*-bromophenylallylhydrazides (CHATTAWAY and TESH), 715.

$C_{17}H_{14}O_3N_2S$ Phenylcarboxy-*o*-tolyl*iso*thiohydantoin (DIXON and KENNEDY), 77.

C_{18} Group.

$C_{18}H_{12}O_2$ Methoxybenzanthrone, and its salts (PERKIN), 698.

$C_{18}H_{14}O_7$ 2:3-Diacetoxy-8-methoxyxanthone, preparation of (DEAN and NIERENSTEIN), 804.

$C_{18}H_{15}As$ Triphenylarsine, preparation of (BURROWS and TURNER), 1382; (POPE and TURNER), 1447.

$C_{18}H_{15}Bi$ Triphenylbismuthine, molecular weight of, and its salts (CHALLENGER and GODDARD), 765.

$C_{18}H_{18}O_6$ 3:5:3′:4′-Tetramethoxy-2-phenylcoumaran-1-one (NIERENSTEIN), 1155.

$C_{18}H_{20}O_7$ 2′-Hydroxy-3:4:4′:6′-tetramethoxydiphenylacetic acid (NIERENSTEIN), 1154.

$C_{18}H_{34}O_2$ Oleic acid, sodium salt, investigations of solutions of, as curd, gel, and sol (LAING and MCBAIN), 1506.

18 III

$C_{18}H_{10}O_5N_4$ 3:4-Dinitroacenaphthenequinone-7-phenylhydrazone (ROWE and DAVIES), 1351.

$C_{18}H_{11}O_3N_3$ 3-Nitroacenaphthenequinone-7(or 8)-phenylhydrazone (ROWE and DAVIES), 1350.

$C_{18}H_{12}O_3N_2$ 1-β-Anthraquinonyl-3-methyl-5-pyrazolone (SAUNDERS), 1268.

$C_{18}H_{12}O_5N_4$ 4-β-Anthraquinoneazo-3-methyl-5-pyrazolone (SAUNDERS), 1270.

$C_{18}H_{16}O_2N_2$ α- and β-Phthalyl-*p*-tolylallylhydrazides (CHATTAWAY and TESH), 716.

$C_{18}H_{16}O_3N_2$ α-Phthalyl-*n*-butyrylphenylhydrazide (CHATTAWAY and TESH), 717.

$C_{18}H_{19}O_3N_5$ Benzoyl derivative of camphorquinonecyanohydrazone (FORSTER and SAVILLE), 756.

$C_{18}H_{21}O_5Cl$ 3:4:2′:4′:6′-Pentamethoxydiphenylmethyl chloride (NIERENSTEIN), 978.

18 IV

$C_{18}H_{13}O_2N_4B$ Boro-α-phenylhydrazidobenzeneazophenol, and its hydrochloride (CHAUDHURI), 1085.

C_{19} Group.

$C_{19}H_{14}O_3$ Dimethoxybenzanthrone, and its salts (PERKIN), 703.

$C_{19}H_{16}N_2$ *o*-Aminocinnamylidenequinaldine, and its dihydrochloride (MILLS and EVANS), 1038.

$C_{19}H_{20}O_2$ Benzoyl derivative of 1-phenyl*cyclo*hexan-3-ol (BOYD, CLIFFORD, and PROBERT), 1388.

$C_{19}H_{22}O_7$ 3:4:2′:4′:6′-Pentamethoxydiphenylacetic acid, and its sodium salt (NIERENSTEIN), 977.

2:4:6:3′:4′-Pentamethoxydiphenylmethane-3-carboxylic acid (NIERENSTEIN), 975.

$C_{19}H_{24}O_5$ 2′-Hydroxy-3:4:4′:6′-tetramethoxy-αα-diphenylpropane (NIERENSTEIN), 1154.

$C_{19}H_{28}O_3$ *l*-Menthyl atrolactinates, and their hydrolysis (MCKENZIE and WREN), 686.

l-Menthyl *d*-α-hydroxy-β-phenylpropionate, and its hydrolysis (MCKENZIE and WREN), 690.

19 III

$C_{19}H_{13}O_2N$ Anilinoxanthone (DHAR), 1068.

$C_{19}H_{14}O_2N_2$ *p*-Nitrocinnamylidenequinaldine (MILLS and EVANS), 1038.

$C_{19}H_{17}O_5N_3$ Triacetyl derivative of azo-colouring matter $C_{13}H_{11}O_5N_3$ (MORGAN and DREW), 791.

$C_{19}H_{15}O_4N_3$ 4-β-Anthraquinoneazo-3-methyl*iso*oxazolone (SAUNDERS), 1272.

$C_{19}H_{19}O_4N$ *o*-Nitrobenzoyl derivative of 1-phenyl*cyclo*hexan-3-ol (BOYD, CLIFFORD, and PROBERT), 1388.

$C_{19}H_{21}O_6Cl$ 3:4:2′:4′:6′-Pentamethoxydiphenylacetyl chloride (NIERENSTEIN), 1153.

C_{20} Group.

$C_{20}H_{14}O_4$ Phenolphthalein, preparation of (COPISAROW), 212.

$C_{20}H_{16}O$ 4-Diphenylyl benzyl ketone (FERRISS and TURNER), 1148.

$C_{20}H_{22}O_8$ 2′-Acetoxy-3:4:4′:6′-tetramethoxydiphenylacetic acid (NIERENSTEIN), 1155.

$C_{20}H_{24}O_6$ 2:4:6-Trimethoxyphenyl 3:4-dimethoxy-β-phenylethyl ketone (NIERENSTEIN), 976.

$C_{20}H_{24}O_7$ Methyl 3:4:2′:4′:6′-pentamethoxydiphenylacetate (NIERENSTEIN), 978.

Methyl 2:4:6:3′:4′-pentamethoxydiphenylmethane-3-carboxylate (NIERENSTEIN), 976.

$C_{20}H_{26}O_5$ 3:4:2′:4′:6′-Pentamethoxy-αα-, and -αγ-diphenylpropanes (NIERENSTEIN), 976, 1153.

2:4:6:3′:4′-Pentamethoxy-3-ethyldiphenylmethane (NIERENSTEIN), 975.

$C_{20}H_{26}O_6$ 2:4:6:3′:4′-Pentamethoxy-3-ethyldiphenylcarbinol (NIERENSTEIN), 974.

$C_{20}H_{27}N_3$ Diazoamino-4-*n*-butylbenzene (REILLY and HICKINBOTTOM), 113.

20 III

$C_{20}H_{14}O_3N_2$ Azine, from 8-hydroxy-2:3-quinoxanthone and 3:4-tolylenediamine (DEAN and NIERENSTEIN), 803.

$C_{20}H_{18}ON_2$ *o*-Formylaminocinnamylidenequinaldine (MILLS and EVANS), 1038.

$C_{20}H_{16}O_5N_2$ Ethyl β-anthraquinoneazoacetoacetate (SAUNDERS), 1271.

$C_{20}H_{19}O_6N_5$ Substance, from *m*-toluidine and tetryl (JAMES, JONES, and LEWIS), 1276.

$C_{20}H_{19}N_2I$ *o*-Aminocinnamylidenequinaldine methiodide (MILLS and EVANS), 1040.

$C_{20}H_{20}ON_2$ 4-*n*-Butylbenzeneazo-β-naphthol (REILLY and HICKINBOTTOM), 113.

$C_{20}H_{20}O_2N_2$ 4-*n*-Butylbenzeneazo-2:7-dihydroxynaphthalene (REILLY and HICKINBOTTOM), 114.

$C_{20}H_{21}IAs$ Diphenylmethylarsine benziodide (BURROWS and TURNER), 1381.

$C_{20}H_{22}O_2N_2$ 4-*n*-Butylbenzeneazobenzoylacetone (REILLY and HICKINBOTTOM), 114.

$C_{20}H_{23}ON$ α- and β-Naphthylaminocamphor, optical rotation of (B. K. and D. Singh, Dutt, and G. Singh), 986.
$C_{20}H_{23}O_6Cl$ 3:4:2′:4′:6′-Pentamethoxydiphenylmethyl chloromethyl ketone (Nierenstein), 1153.
$C_{20}H_{24}O_2N_2$ Quinine, ferrocyanides of (Briggs), 1034.
$C_{20}H_{25}ON$ *ar*-Tetrahydro-α-naphthyliminocamphor, preparation and rotation of (B. K. and D. Singh, Dutt, and G. Singh), 987.
$C_{20}H_{27}ON$ *ar*-Tetrahydro-α-naphthylaminocamphor (B. K. and D. Singh, Dutt, and G. Singh), 987.

20 V

$C_{20}H_{21}ON_4Cl_2Co$ Dichlorotetrapyridinecobalt hydroxide, salts of (Price), 860.

C_{21} Group.

$C_{21}H_{14}O_5$ Diacetoxybenzanthrone (Perkin), 701.
$C_{21}H_{21}As$ Tri-*o*-tolylarsine (Burrows and Turner), 1382.
$C_{21}H_{22}O_5$ Apigenin triethyl ether, salts of (Perkin), 699.
$C_{21}H_{30}O_6$ Methyl derivative of 2:4:6:3′:4′-pentamethoxy-3-ethyldiphenylcarbinol (Nierenstein), 974.

21 III

$C_{21}H_{13}N_3Cl$ Chloromethylbenzophenanthrazines (Morgan and Drew), 789.
$C_{21}H_{18}ON_2$ *o*-Acetylaminocinnamylidenequinaldine (Mills and Evans), 1039.
$C_{21}H_{18}O_3N_2$ Carboxymethylaminocinnamylidenequinaldine (Mills and Evans), 1039.
$C_{21}H_{21}O_6N_3$ Tetra-acetyl derivative of 4-nitro-2:4′-diaminodiphenylmethane (King), 990.
$C_{21}H_{22}O_2N_2$ Dianilide of *trans-cyclo*pentane*spirocyclo*propane-1:2-dicarboxylic acid (Becker and Thorpe), 1587.
$C_{21}H_{26}O_4N_2$ Ethyl 4-*p*-dimethylaminophenyl-2:6-dimethylpyridinedicarboxylate, and its potassium salt (Hinkel and Cremer), 139.
$C_{21}H_{28}O_4N_2$ Ethyl 4-*p*-dimethylaminophenyl-2:6-dimethyl-1:4-dihydropyridine-3:5-dicarboxylate, and its salts (Hinkel and Cremer), 138.

21 IV

$C_{21}H_{13}O_3N_2Br$ α-Phthalylbenzoyl-*p*-bromophenylhydrazide (Chattaway and Tesh) 718.

C_{22} Group.

$C_{22}H_{16}O_2$ 2:7-Dimethylfluoran, preparation of (Copisarow), 215.
$C_{22}H_{16}O_4$ *o*-Cresolphthalein, preparation of (Copisarow), 214.
$C_{22}H_{28}O_7$ Acetyl derivative of 2:4:6:3′:4′-pentamethoxy-3-ethyldiphenylcarbinol (Nierenstein), 974.

22 III

$C_{22}H_{16}O_3N_2$ α-Phthalylbenzoyltolylhydrazides (Chattaway and Tesh), 718.
$C_{22}H_{17}Br_2Bi$ Diphenyl-α-naphthylbismuthine dibromide (Challenger and Goddard), 772.
$C_{22}H_{20}ON_2$ Benzoyl*iso*propylidenebenzidine (Ferris and Turner), 1146.
$C_{22}H_{24}IAs$ Tri-*o*-tolylarsine methiodide (Burrows and Turner), 1382.

22 IV

$C_{22}H_{21}ON_2I$ Acetylaminocinnamylidenequinaldine methiodide (Mills and Evans), 1039.

C_{23} Group.

$C_{23}H_{20}O_6$ Luteolin tetraethyl ether, salts of (Perkin), 699.

23 III

$C_{23}H_{13}O_7N_4$ Dinitroxanthoneazo-β-naphthol (Dhar), 1064.

C_{24} Group.

$C_{24}H_{22}N_2$ 2:3-Diphenyl-6-*n*-butylquinoxaline (Reilly and Hickinbottom), 118.

$C_{24}H_{24}N_2$ 2:4:8:2′:4′:8′-Hexamethyl-6:6′-diquinolyl, and its platinichloride (Ferris and Turner), 1146.

$C_{24}H_{36}O_6$ Dibornyl tartrates (Wren, Williams, and Myddleton), 193.

$C_{24}H_{50}O$ Alcohol, from *Hyenanche globosa* (Henry), 1624.

24 III

$C_{24}H_{13}O_5N_3$ 3-Nitroanthraquinone-1-azo-β-naphthol (Dhar), 1003.

$C_{24}H_{16}O_3N_4$ 4-Benzeneazo-1-β-anthraquinonyl-3-methyl-5-pyrazolone (Saunders), 1268.

$C_{24}H_{24}ON_2$ Benzoyl*iso*propylidenetolidine (Ferriss and Turner), 1147.

$C_{24}H_{28}O_2N_2$ Diacetyl*iso*propylidenetolidine (Ferriss and Turner), 1146.

C_{25} Group.

$C_{25}H_{25}O_3N_3$ Tribenzoyl derivative of diethylenetriamine (Fargher), 1354.

$C_{25}H_{25}N_2Br$ 1:1′-Diethylcarbocyanine bromide (Mills and Hamer), 1558.

$C_{25}H_{25}N_2I$ 1:1′-Diethylcarbocyanine iodide (Mills and Hamer), 1557.

25 IV

$C_{25}H_{29}O_4N_4Br$ Substance $(+ 2H_2O)$ from oxidation of 1:1′-diethylcarbocyanine bromide with nitric acid (Mills and Hamer), 1561.

C_{26} Group.

$C_{26}H_{22}O_{11}$ Acetyl derivative of 5:7:2′:4′:6′-pentahydroxy-2-phenyl-4-methylene-1:4-benzopyran (Sen and Ghosh), 62.

$C_{26}H_{25}N_3$ 4-*n*-Butylbenzeneazophenyl-β-naphthylamine (Reilly and Hickinbottom), 113.

$C_{26}H_{52}O_2$ Acetyl derivative of alcohol $C_{24}H_{50}O$ (Henry), 1624.

26 III

$C_{26}H_{31}O_3N_3$ Acetyl*iso*propylidenetolidine (Ferriss and Turner), 1145.

$C_{26}H_{36}O_2N_2$ *m*-Phenylenebisaminocamphor (B. K. and D. Singh, Dutt, and G. Singh), 985.

C_{27} Group.

$C_{27}H_{34}O_8$ Myricetin hexaethyl ether, salts of (Perkin), 699.

27 III

$C_{27}H_{33}O_3N_3$ Acetyl*iso*propylidenebenzoyl*iso*propylidenebenzidine (Ferriss and Turner), 1146.

$C_{27}H_{34}O_2N_2$ *m*-Tolylenebisiminocamphor, preparation and rotation of (B. K. and D. Singh, Dutt, and G. Singh), 984.

$C_{27}H_{36}O_2N_2$ *m*-Tolylenebisaminocamphor, preparation and rotation of (B. K. and D. Singh, Dutt, and G. Singh), 985.

C_{28} Group.

$C_{28}H_{24}$ Dimethyl-9:10-diphenyl-9:10-dihydroanthracene (RÂY), 1338.

28 II

$C_{28}H_{16}O_2$ α- and β-Naphthafluorans, and α-Naphtholphthaleins, preparation of (COPISAROW), 216.

$C_{28}H_{22}O_2$ 4:4′-Diphenyldiacetyldiphenyl (FERRISS and TURNER), 1150.

$C_{28}H_{24}O_2$ Diacetyl derivative of 9:10-diphenyl-9:10-dihydroanthracene (RÂY), 1337.

$C_{28}H_{46}O$ Phytosterol from *Hyenanche globosa* (HENRY), 1624.

28 III

$C_{28}H_{18}O_3N_4$ 4-β-Anthraquinoneazo-1-β-naphthyl-3-methyl-5-pyrazolone (SAUNDERS), 1271.

4-α-and-β-Naphthaleneazo-1-β-anthraquinonyl-3-methyl-5-pyrazolones (SAUNDERS), 1269.

C_{30} Group.

$C_{30}H_{28}$ Dimethyl-9:10-ditolyl-9:10-dihydroanthracene (RÂY), 1338.

30 II

$C_{30}H_{48}O_2$ Acetyl derivative of phytosterol $C_{28}H_{46}O$ (HENRY), 1624.

30 III

$C_{30}H_{22}Cl_2Bi$ Tri-α-naphthylbismuthine dichloride (CHALLENGER and GODDARD), 772.

$C_{30}H_{24}O_2N_2$ 1:4-Naphthylenebisiminocamphor (B. K. and M. SINGH), 1599.

C_{31} Group.

$C_{31}H_{24}O_4N_4$ Phthalylphenyltrimethylenebishydrazide (CHATTAWAY and TESH), 714.

C_{32} Group.

$C_{32}H_{18}O_5N_4$ 4-β-Anthraquinoneazo-1β-anthraquinonyl-3-methyl-5-pyrazolone (SAUNDERS), 1269.

C_{37} Group.

$C_{37}H_{25}N_3$ Tri-3-carbazylmethane (COPISAROW), 1546.

37 III

$C_{37}H_{24}N_3Cl$ Tri-3-carbazylcarbinyl chloride (COPISAROW), 1546.

$C_{37}H_{25}ON_3$ Tri-3-carbazylcarbinol (COPISAROW), 1545.

C_{38} Group.

$C_{38}H_{28}$ 9:9:10:10-Tetraphenyl-9:10-dihydroanthracene (RÂY), 1339.

38 III

$C_{38}H_{25}O_2N_3$ Carbazole-blue or Tri-3-carbazylcarbinyl formate (COPISAROW), 1546.

C_{43} Group.

$C_{43}H_{27}N_3$ Tri-9-ethyltri-3-carbazylmethane (COPISAROW), 1548.

43 III

$C_{43}H_{26}N_3Cl$ Tri-9-ethyltri-3-carbazylcarbinyl chloride (COPISAROW), 1548.

$C_{43}H_{27}ON_3$ Tri-9-ethyltri-3-carbazylcarbinol (COPISAROW), 1549.

C_{44} Group.

$C_{44}H_{27}O_2N_3$ Carbazole-violet or Tri-9-ethyltri-3-carbazylcarbinyl formate (COPISAROW), 1547.